



## Official Notice.

### REPORTS OF THE PROGRESS OF APPLIED CHEMISTRY.

The first volume of the Reports of the Progress of Applied Chemistry is now in active preparation, and will, it is hoped, be published in December. It will cover recent progress to the end of June, 1916. The second volume will deal with the period up to the end of 1917, and subsequently it is proposed to issue the Reports annually.

The Reports will present a critical summary of the progress that has been made in the various branches of chemical industry during the period in question. It has not been found practicable to treat every section of the Journal classification. Agricultural chemistry, the chemistry of foods, and analysis are fully dealt with in the admirable series of Reports issued annually by the Chemical Society, and for the present there will be no sections on general plant and explosives.

The following is a list of the subjects which will be dealt with, together with the names of the experts who are contributing to this volume:—

- Fuel*—J. W. Cobb, B.Sc., F.I.C.
- Gas, destructive distillation, tar products*—E. V. Evans, F.I.C.
- Mineral oils*—A. W. Eastlake.
- Dyestuffs*—G. T. Morgan, D.Sc., F.I.C., F.R.S.
- Fibres, paper, dyeing, printing*—Julius Huebner, F.I.C.
- Acids, alkalis, salts, etc.*—H. A. Auden, Ph.D., F.I.C.
- Glass, ceramics, cement, etc.*—J. A. Audley, B.Sc.
- Metals, metallurgy*—W. R. E. Hodgkinson, Ph.D., F.I.C.
- Electro-chemistry*—J. T. Barker, Ph.D.
- Fats, oils, waxes*—G. H. Warburton.
- Paints, pigments, varnishes, resins*—R. S. Morrell, M.A., Ph.D.
- Indiarubber*—H. P. Stevens, M.A., Ph.D., F.I.C.
- Leather, glue, etc.*—J. T. Wood, F.I.C.
- Sugar, starches*—J. G. Macintosh.
- Fermentation*—A. R. Ling, F.I.C.
- Sanitation, water purification*—F. R. O'Shaughnessy, F.I.C.
- Fine chemicals, medicinal substances, essential oils*—F. L. Pyman, D.Sc., Ph.D.
- Photographic materials and processes*—B. V. Storr, M.Sc.

The price of issue will be, to members, 2s. 6d. plus 6d. postage, and non-members, 5s. (plus 6d. postage). As the issue is to be a limited one, those desirous of securing copies are requested to fill in the order form attached to the cover of the Journal, and return it to the Secretary at an early date.

## Editorial.

### SCIENCE AND TRADE.

The *Daily Telegraph* recently published an article by Sir Robert Hadfield with the above title, dealing with the necessity for research in industry, and calling special attention to the importance of co-ordination in research, and to the need for constant investigation of what is being achieved abroad and for the encouragement of pure science. Emphasising the vital necessity for co-ordination, Sir Robert says that if British industry is to hold its own after the war, research must be regarded as a national rather than an individual

matter. While big firms naturally maintain their own laboratories for research along the lines of their special activities, and many of the results obtained in these laboratories are of special interest to themselves, there are a great number of questions affecting whole industries the solution of which can only be obtained by the co-operation of many workers investigating special branches of the subject. In these cases there is everything to be gained by carrying on the work of research in combination and making its results available to the whole of the organised industry.

It was announced last month that the National Research Council recently appointed by the American National Academy of Sciences to co-ordinate scientific research in the United States, had received an assurance that the funds and organisation of the Engineering Foundation would be placed at its disposal. In order to ensure practical application of all discoveries made, the great engineering societies will be strongly represented on the council.

The council also contains the names of the leading scientists in the American universities and representatives of important service and Government departments such as the directors of Ordnance and Aviation, of the National Bureau of Standards, and the Bureau of Mines. Thus, the effect of the council is to co-ordinate the work of the finest pure scientists in the United States with every important branch of national life and industry to which the results of research can be applied. It is obvious that such a combination should do much to achieve the object for which the council was established, to put the United States in the forefront of the nations in the application of science to industry or warfare.

We certainly can do much here. In the Iron and Steel Institute and similar organisations we have technical institutions as progressive as any in the world, and our scientists are in no way inferior to the best of foreign countries. It is noteworthy that Dr. G. E. Hale, the chairman of the American Research Council, and Dr. W. H. Welch, president of the National Academy of Sciences, have recently been visiting this country to see what was being accomplished in the way of scientific research, and they have returned full of praise for the work in progress and ready to hold it up as an example to their own countrymen. Dr. Hale particularly called attention to the work which pure scientists were doing on the solution of common problems, instancing the work on optical glasses carried out by Professor Jackson, of King's College, London.

All that is needed is a better co-ordination of our resources. The appointment of the Advisory Council for Scientific and Industrial Research is a first right step. It is of prime importance that the State should be ready to co-operate by bringing educational requirements up to date, by providing proper equipment for laboratories and technical colleges, and by grants in aid for the encouragement of research. But the industries must do their part. There has in the past been perhaps a little too much jealousy and unwillingness to co-operate for common ends, which must give place in the future to a great combined effort to raise the whole level of British industry. Too many of our splendid technical institutions, also, are to-day insufficiently endowed and ill-provided with centres, libraries, and appliances. If, for instance, we could bring the chief metallurgical, mining, and engineering societies under a common roof and organise their activities in co-operation with all kindred institutions throughout the country, their

united power would form a most valuable factor in the promotion of research on a national scale.

Such tours of inspection as that made by Dr. Hale and Dr. Welch in this country have a great value in keeping the science and industry of a nation abreast of the latest developments all over the world and suggesting fresh lines of activity and fresh subjects for investigation.

Lastly, in our desire to obtain practical results we should not confine research to problems of immediate practical utility. Even from the commercial point of view we shall do well to provide every possible facility and encouragement for the toiler in pure science. Many of our greatest advances in trade and industry are due to incidental discoveries made in the course of purely theoretical research, which seemed at the time to serve no particular practical purpose. Thus we are to-day reaping the benefit of the careful observations made by the late Dr. Gore nearly fifty years ago of the extraordinary changes produced in iron and steel by temperatures of, say, 300° C. and upwards. Yet many years passed before these observations were turned to practical account.

The special equipment and capacities of the pure scientist can only be obtained by encouraging him to work on his own lines and for sheer love of the work. What is needed is to render the results which he obtains more readily available to the technical worker, who can then himself follow up, or request the co-operation of the scientist in following up, those discoveries which give the most prospect of commercially useful results.

Even in works laboratories it is well to encourage pure experiment in regard to all materials used in industry, without regard to immediate application. The trained observer, watching the effect of new combinations and processes, may at any time find that the notes in his experiment book give him the clue to discoveries of the first importance. It was in the course of such experiments that the clues were obtained which led to the discovery of manganese steel, which is now used on almost every steam railroad and street tramway in the world, and is largely responsible for the efficiency of modern mining machinery, and its latest use has been found in the manufacture of steel helmets for our soldiers at the front. In a similar way experiments led to the utilisation of what is known as low hysteresis material, which represents a peculiar combination of elements and heat treatment. This knowledge has been applied to transformers throughout the world, with a resulting decrease in energy losses which is saving millions of pounds each year.

#### SOCIETY OF GLASS TECHNOLOGY.

The Society of Glass Technology was formally constituted at a largely attended meeting held at Sheffield University on November 9th. Representatives of the industry from all the glass-manufacturing districts of Great Britain were present. It was pointed out that the glass industry, among others, had suffered in the past owing to its detachment—partial or entire—from its scientific aspects. The formation of the Department of Glass Technology in the University of Sheffield was serving to remedy this state of affairs, and the inauguration of the Society was a further step in the same direction. It was to be hoped that the Society would be an active force not only in this country but throughout Europe. Dr. W. E. S. Turner outlined the steps that had led up to the formation of the Society, and said that promises of support had been received from all over the country. The Society was not to be a local institution, but a national one in every way, and meetings would be held from time to time in various centres.

The report of the Provisional Committee was adopted and a formal resolution constituting the Society was passed. Mr. W. F. J. Wood was elected President for the coming year, and Dr. W. E. S. Turner, of the University, Sheffield, Secretary, from whom further information may be obtained.

#### THE ACTION OF SOLVENTS ON COAL.

The earlier attempts to extract the soluble or resinoid constituents of coal by means of solvents met with little success. Alcohol, ether, chloroform, benzene, and acetone were tried, but ordinary bituminous coals yielded only about 1% or less to the solvent, though Watson Smith (this J., 1891, 975; 1892, 591; 1893, 221) recorded the fact that the remarkable Miike coal of Japan yields nearly 10% of its weight to benzene extraction, and Smythe (see this J., 1908, 149) by successive extractions with several solvents of low boiling point, succeeded in extracting over 7% from German brown coal. Recently (this J., 1916, 1001) Fischer and Glud have shown that the yield of benzene extract is greatly increased at high temperatures and pressures (e.g., 275° C. and 55 atm.): under these conditions ordinary coal yielded 61% extract as compared with 0.1 to 0.15% at 80° C.; lignite 25% as against 11%, and cannel coal 4% as against 1%.

The high solvent action of pyridine on coal was first noted by Bedson (this J., 1899, 739), who found that Durham coal yielded from 16 to 18% and New Zealand coal from 10 to 13% of soluble matter. Anthracites are unaffected by the solvent. Later (this J., 1901, 789), Baker examined the solvent action on coal of the fraction of pyridine bases boiling between 110° and 120° C., the powdered coal being extracted in a Soxhlet apparatus; samples of Durham coals, from the Hutton and Brockwell seams, yielded 20.4 and 11.5% of extract respectively, and a New Zealand coal furnished 21.4%, but of this 15.75% consisted of water. In each case the residue had lost the coking properties of the original coal, either entirely or to a very large extent. In a later communication (this J., 1908, 147), Bedson gives the results of the extraction of some gas coals with pyridine; the extracts represented from 22.53 to 33.59% of the coal substance, and attention is drawn to the apparent approximation between the amount yielded to pyridine and the percentage of "volatile matter." Similar treatment of four coals described as "cannels" yielded respectively 6.95, 8.31, 26.05, and 28.90% of extract, whilst a specimen of Broxburn oil shale furnished only 1.59%. Bedson states that the extracted substance, which is a dark, resinous, scaly solid, had been submitted to extraction with light solvents, and that the petroleum ether extract yielded a substance volatile in steam, the ether extract of the distillate furnishing a product which forms transparent red crystals, m.pt. 65° C. The ether extract also yielded a substance volatile in steam, and a basic and an acidic substance. Full details are promised, but no further communication has apparently been made on the subject.

Pyridine is not the only substance which has a high solvent action on coal constituents. Thus, Vignon (this J., 1914, 633) states that aniline dissolved 23.4% and quinoline 47.3% (at boiling point) of a bituminous gas coal from the Loire district, whilst Parr and Hadley (this J., 1915, 213) record the extraction of 35 to 40% from "high volatile" coal and 20 to 30% from "low-volatile" coal by treatment with phenol at 110° C. in an atmosphere of carbon dioxide.

The researches of Burgess, Wheeler, and Clark (this J., 1910, 1291; 1911, 606; 1913, 969) have led to the view that coal is essentially a conglomerate of degradation products of cellulose, and partly

changed resins and gums of the plants from which the coal was derived. Extraction with pyridine effects only a partial separation of the two constituents, but a complete or nearly complete separation can be made by extraction with pyridine and treatment of the pyridine extract with chloroform. The properties of the residues from each of these extractions are similar, and have no effect on a photographic plate, but the portion of the pyridine extract soluble in chloroform has a marked action, similar to that produced by rosin and coal itself (cf. Russell, this J., 1908, 959). The residue from the extraction with pyridine, on distillation at 900° C., yielded chiefly hydrogen, carbon monoxide, and carbon dioxide, whilst the pyridine extract yielded paraffin hydrocarbons and hydrogen, the percentage of the latter increasing with the temperature. The chloroform extract of the pyridine fraction (about one-third of its weight) contains 80% of volatile matter and on distillation yielded 43 to 64.5% of tar, consisting mainly of paraffin hydrocarbons, together with gases consisting principally of hydrogen and paraffin hydrocarbons. It was further established by the same authors that in the distillation of coals at low temperatures (up to 450°–500° C.) higher paraffins, as well as methane, are conspicuous decomposition products, whereas hydrogen is produced in very small quantity; the evolution of paraffins ceases entirely at about 700° C., whilst between 700° and 800° C. there is a well-defined point at which the evolution of hydrogen shows a marked increase. It would thus seem probable that the constituents of the coal derived from gums and resins are the less stable ones, which yield paraffins on distillation, whilst the cellulosic degradation product is the more stable, hydrogen-yielding constituent. Further confirmation of this view was afforded by the work of Jones and Wheeler (this J., 1915, 1043), who found that the chloroform extract yielded a tar free from phenols, whilst the products obtained by distillation of the residue from pyridine extraction and from the chloroform extraction of the pyridine extract, contained phenols—a characteristic of celluloses and degraded cellulose derivatives. Harger (this J., 1914, 390) considers that the portions extracted by pyridine are somewhat modified in constitution by the process (as indicated by the fact that extraction is very slow and is accelerated by increased temperatures), just as many resins are rendered soluble only after heating.

As regards the actual identity of the constituents of coal little of a definite nature is known. Pictet and Ramsayer (this J., 1911, 1041) isolated hexahydrofluorene,  $C_{12}H_{10}$ , by extraction with benzene, and Pictet, Ramsayer, and Kaiser have recently separated fourteen other saturated and unsaturated hydrocarbons from the benzene extract (see page 1145). These compounds, however, are present in such minute proportions that their isolation must be considered to be of purely theoretical interest. The cellulosic portion consists of compounds of the furane type (Jones and Wheeler, this J., 1916, 881); and compounds having structures similar to that of the carbon molecule are also present, but it is improbable that coal contains free elementary carbon. The resinic constituents are considered to consist of compounds in which alkyl, naphthene, and hydro-aromatic groupings are attached to more complex groupings. The oxygenated resinic derivatives are probably chiefly cyclic oxides, and esters, ketones, acids, etc., are almost completely absent. Free hydrocarbons are present in small quantities, but it is doubtful whether aromatic groupings exist.

From the above brief summary it will be evident that, while a considerable amount of work has been done towards elucidating the chemical nature of coal, very much remains to be accomplished before

we can lay claim to a definite knowledge of the composition of the most important of our mineral resources.

#### THE MESSERSCHMITT PROCESS FOR MAKING HYDROGEN.

In a recent issue of *Metallurgical and Chemical Engineering* H. L. Barnitz gives some interesting details of the Messerschmitt process for the production of hydrogen, the information having been received direct from the inventor. Additional importance is added to the subject in view of the statement that the German military authorities have adopted this process in preference to all others for use in large installations. The German War Department now controls fourteen Messerschmitt plants, each having a capacity of from 100 to 600 cubic metres per hour, and erected at a cost of about £1,000,000.

The process is based on the old iron-contact method, and consists broadly in passing steam over heated iron and subsequently reducing the iron oxide by means of reducing gases—water-gas, producer gas, or coal gas. The latest type of generator consists of an upright, cylindrical shaft, lined with fire-brick, and having two concentric iron cylinders built into it, the smaller of the cylinders resting on the floor of the generator, whilst the larger cylinder is supported at a short distance from the floor, to leave a space for the admission of the steam or reducing gas to the contact mass, which is packed into the annular space between the two cylinders. The inner cylinder contains a cage-work of fire-brick which serves to store the heat required to bring the contact mass to the reaction temperature. The outer cylinder is also surrounded by a fire-brick caging, which is incorporated in the construction of the outer fire-brick mantle of the shaft. The heating of the fire-brick cage-work and the heating and reduction of the contact mass are effected by introducing reducing gases and air from beneath into the inner cylinder; the proportion of air used is not sufficient for the complete combustion of the gases.

In the first stage of the process—the heating and reduction stage—the mixture of water-gas and air is partly burnt in the inner cylinder and the combustion products, with the unconsumed portion of the gas, pass downwards through the contact mass (the inner cylinder being cut off short of the top of the generator shaft), and then again upwards around the outer cylinder, through the flue, and into the open. During the passage of the gases around the outer cylinder the unconsumed portion is burnt by means of a secondary air current, introduced through the upper part of the wall of the shaft. This heating and reduction process occupies about twenty minutes, a temperature of 700°–800° C. being necessary.

At this stage the supply of air and gas is cut off and steam is blown in from below the generator, driving the carbon dioxide produced from the contact mass into the exit flue. As soon as hydrogen is seen to escape with the steam, the steam supply from below is cut off and the ventilator leading to the flue is closed. This second, or steam-rinsing stage only occupies a few seconds.

In the third, or actual hydrogen-producing stage, steam is passed into the top of the space between the outer cylinder and the shaft casing, and traverses the generator in the opposite direction, passing upwards through the glowing contact mass, where it is decomposed, and the hydrogen is taken off at the top into a chamber provided with a water-seal. From this chamber the gas is passed through a purifier into the gas-holder and is then compressed into cylinders or storage tanks. The producing period is of about 15 minutes' duration.

The entire process is then repeated, again introducing air and water.

The hydrogen is purified by passing the water to remove dust particles, and then through a purifier containing lime to remove traces of sulphur dioxide and carbon dioxide. The gas is then dried (99.2%) and to contain only 0.8% of water.

Among the advantages claimed are that over-heating is easily avoided, the necessary temperature of the contact mass can be maintained without difficulty, the gas consumption is very low, a single water-gas generator and steam boiler being sufficient for several hydrogen generators. The actual cost of the hydrogen is governed by the cost of coke and the size of the apparatus. In one plant installed in the United States, where the process is in use for producing hydrogen for treating oils, the cost has averaged 40 to 45 cents (1s. 8d. to 1s. 10d.) per 1000 cu. ft.; these figures include interest, depreciation, and labour. The labour item is very small, since one man is able to attend to two generators, his sole duty being to change the levers for each working period and to read the pyrometer. All lever positions are automatically locked, thus preventing wrong position of ventilators.

When the contact mass requires to be renewed, it is removed through Morton doors provided in the lower part of the shaft casing, whilst fresh material is introduced through openings arranged on the top of the generator.

The first patents for this process were taken out by Messerschmitt in Germany in 1911; his inventions have been referred to in this Journal, 1912, 1126; 1913, 944; 1914, 136, 137, 313; 1915, 1010.

#### HYDROGEN FOR MILITARY PURPOSES.

Though the iron-contact process is probably the cheapest method for producing hydrogen, several of the other processes possess advantages in regard to portability of apparatus, etc., when the gas is required for military purposes. The comparative figures as to the cost of the various processes, given by E. D. Ardery at a recent meeting of the American Electrochemical Society, are therefore of considerable interest.

The results of this comparison show that the price per cubic metre of hydrogen is:—Action of steam on iron, 1.5d.; distillation of crude oil and tar, 1.75d.; ferrosilicon, 10d.; water-gas, 1s. 0d.; iron and sulphuric acid, 1s. 0d.; hydrogenit, 1s. 4d.; hydrolith (calcium hydride), 3s. 8d. to 4s. 2d.; silicon and caustic soda, 4s. 5d.

In the Russo-Japanese war the Russians used a process based on the action of caustic soda on aluminium; the disadvantage of this method was that it required 5½ kilos. of raw materials to produce a cubic metre of gas, as against about 4½ kilos. when using the sulphuric acid and iron or zinc process. In the Morocco campaign, the Spanish Government produced the hydrogen required by the action of caustic soda solution on silicon at 80° to 90° C.; the apparatus required is made of iron, is very simple in construction, and very durable.

The ferrosilicon process has been used by the French, and also the "hydrogenit" process. "Hydrogenit" is a mixture of finely powdered ferrosilicon and soda-lime, and is especially adapted for use where water is not abundant; on ignition it yields hydrogen.

The calcium hydride process is too expensive for general use: one kilo. of the hydride yields about one cubic metre of hydrogen. A lead-sodium alloy, called "hydrona," has also been introduced for producing hydrogen by the action of water.

A process which has been used both in Russia

and in Germany consists in passing the gases produced during the distillation of crude oil and tar, through a mass of hot coke; the hydrogen thus produced contains 2—3% of carbon monoxide; the process is intermittent, but is inexpensive.

The United States Army has installed a plant for producing hydrogen by the electrolysis of water; a direct current of 1500 amperes at 85 to 120 volts is passed through thirty cells connected in series. The capacity of the plant is about 3000 cubic feet per hour.

For carrying the hydrogen from the works to the point of use, the U.S. service employs cylinders about 7 ft. long by 5½ in. diameter and 4 ft. long by 8½ in. diameter; they are made of cold-drawn seamless steel tubing. Some of the French cylinders are about 4 metres long, 270 mm. internal diameter, and 9 mm. thick. The cylinders generally used in the French service contain 200 litres of gas at a pressure of 133 kilos., equivalent to about 25 cub. metres at atmospheric pressure. In Germany cylinders holding about 36 litres of gas at 130 atmos. pressure are used; these correspond to about 5 cub. metres of balloon space.

A pipe line for carrying hydrogen is in successful operation in Germany. It is 4½ kilometres long and can supply 1000 cubic metres of gas daily.

## Communications.

### COCONUT TODDY IN CEYLON.

BY K. C. BROWNING, M.A., AND C. T. SYMONS, B.A.  
(Government Analyst's Laboratory, Colombo.)

An attempt has been made in this paper to give some account of the constituents of toddy (palm juice) as drawn from the coconut palm (*Cocos nucifera*) in Ceylon. Since the product is a vegetable juice, and since the climate in this Island is so variable, it is only to be expected that the analytical figures should show considerable variations.

As will be seen from the figures given in the third section, the industry which has grown up in connection with this product is a very considerable one, providing employment for comparatively large numbers of people and involving a fairly considerable capital in the Island. With the exception of a paper by H. D. Gibbs,\* and referring to the Philippine Islands alone, the present authors have been unable to find in recent scientific literature details of any exact analyses or examination of the product in question. Details are available for toddy (Tari) drawn from other palms. Such palm juice is largely used in India for making crude sugar; but the palms used in that country appear to be limited to the Date Palm (*Phoenix sylvestris*), the Palmyrah (*Borassus flabelliformis*), and the Kitul (*Caryota urens*).

Hence it appears advisable that these figures should be placed on record. They must, however, be taken as referring only to Ceylon, but, as will be seen later, no very marked differences appear to exist between the Philippine and the Ceylon products.

An account is also given of the method of drawing toddy in Ceylon, and in addition some details as to the various organisms which have been found in fermented toddy. This biological work was largely carried out by one of us in the Jørgensen Laboratory at Copenhagen, using dried samples of toddy sent from Ceylon. It is hoped later to publish some further results on this part of the subject after the examination of fresh samples in Ceylon.

\* Philippine Journal of Science, 1911, 6, No. 3. See this Journal, 1911, 1135.

*Method of drawing toddy.*

As mentioned above, this paper is limited to coconut toddy, and as the method of drawing toddy from this palm differs somewhat from that in use with other palms, a short description of the manner in which this is carried out in Ceylon is included in this section.

The part of the palm used for the purpose is the unopened flower spathe. This is prepared by the drawer ("tapper") for a considerable time (up to one month) before the juice actually begins to flow. The tapper, who is often a Cochin immigrant from Southern India, is scantily clad and carries fastened round his waist a belt which holds a broad tapping knife, a mallet of hard wood (vernac.: Keppetiya) or a piece of buffalo horn or bone weighted with lead, a small pot made of a half coconut shell containing a mixture of crushed leaves, etc., described below, an earthenware pot (chatty) or a gourd with cord attached, and a tin containing his tapping licence. To climb the tree he may make use of bits of coconut husk which have been fastened previously to the tree trunk in the form of a primitive ladder. If these are not available he passes a small loop of fibre round both his ankles to hold his feet close together. With this simple apparatus he works his way up the tree, clasping the trunk between the soles of his feet (as a looped caterpillar clasps a small twig between its tail claspers), and holding the trunk with his arms. When he reaches the crown of the tree, he settles himself on one of the larger leaves and sets about his work.

If he is preparing a new spathe he merely bruises this with his mallet (making a noise like a woodpecker busily searching for a grub). The spathe is bound round with a few strands of fibre, etc., to prevent it from opening out prematurely. When the spathe is nearly ready to produce toddy, the tapper cuts off a small portion from the free end of the spathe, and places a chatty on the end, the pot remaining in position by its own weight. A spathe which is just coming into flower has its free end considerably higher than the other end. Hence any juice flowing from the cut end would naturally trickle down the stem and not into the pot. In order to obviate this difficulty the Sinhalese tappers when preparing a spathe, gradually bend down the free end, so that by the time it comes into use it is at such an angle that the juice will flow into the pot.

The Cochin tappers, who alone use bruised leaves, etc., to smear the cut end, are said to accomplish the same effect by the use of this greasy or mucilaginous mixture without bending the spathe. The application of the mixture appears to have also another purpose as mentioned below. For the first few days of the tapping of a new spathe very little juice flows. When the juice starts to flow freely, the tapper visits the tree once or twice (in exceptional cases three times) a day, removes the collecting chatty, pours the contents into the pot he himself carries, and lets this down by rope to the ground to be collected into a larger vessel by his assistant who remains on the ground. The tapper then takes out his knife and shaves a thin slice off the end of the spathe, taps the end with his mallet, and if he is a Cochin, smears the newly cut portion with the mixture of bruised leaves, etc., and replaces the collecting pot. This application is said to make the juice run more freely by preventing the rapid healing of the wound.

The leaves, etc., used in this mixture by the Cochins belong to several species. The mass usually includes cinnamon leaves (*Cinnamomum Zeylanicum*).

The substances used are lime (mineral), lime fruit (citrus), leaves of cinnamon (vernac.: "Kurundu"), wild cinnamon (*Lilacea Zeylanica*, vernac.: "Davul Kurundu"), shoe flower (*Hibiscus fur-*

*catus*, vernac.: Naabritta), other species of *Hibiscus*, *Aporosa* species, and *Eriodendron anfructuosum* (vernac.: Imbul).

In a *tope* (garden) the trees which are being tapped are usually "coupled" together by means of several strands of coir rope stretching from the top of one tree to the top of the next, so that the tapper may walk on this somewhat frail bridge from tree to tree, and thus save himself the trouble and time of an arduous climb and descent for each tree. In this way a tapper, using coupled trees, may be able to manage as many as a hundred trees per diem, whereas the same tapper could only work about thirty-five if they were not so coupled.

A Sinhalese tapper appears to be able to manage two or three times as many trees as a Cochin tapper. But the Cochin appears to be the more satisfactory of the two so far as yield per tree, etc., is concerned and is thus usually preferred by the tree owners.

Tappers are paid according to the amount of toddy collected. The collecting pots are usually left on the trees for twenty-four hours before the toddy is collected and taken away, even though the spathe has been prepared and cut twice in the day. The methods of tapping, etc., described above appear to have been in use from time immemorial. Robert Knox, who was a captive in the Island for 20 years from 1660, gives in his book an account which agrees almost exactly with the above.

The yield of toddy per tree varies very considerably in the various districts in Ceylon, but cannot at present be correlated with any particular variation in elevation or humidity.

With one tapping per diem, the average daily yield per tree varies from about 600 c.c. at Kurunegala on the border of the dry zone to about 1200 c.c. at Colombo, Mawanella, and Anuradhapura, the last place being actually in the dry inland zone and the others on the moister West coast. With two tapplings the average daily yield varies from 600 c.c. at Matara in the South, to nearly 3000 c.c. at Mawanella, mentioned above. Three tapplings per diem appear to give better results in some places, e.g. at Hattton (wet), where nearly 3500 c.c. are obtained per diem by this method.

The maxima and minima are also very variable. The greatest maximum recorded is 4738 c.c., or more than a gallon, at Hattton, whereas the lowest maximum is just over 1100 c.c., at Hattnapura, also in the wet zone. The lowest minimum, exclusive of records taken when a new spathe was being started, was about 190 c.c.

It is generally agreed that the best yield is obtained when the weather is neither very wet nor very dry. Along the coast it is noticed that trees near the sea yield better than those further inland.

With reference to the age of the tree, the following is an extract from a report from the Distillery district:—

"Vigorous trees of between 20 or 30 years of age are believed to yield best. . . . In my experience no rule can be laid down with regard to the age of the trees. Very old trees (more than 80 years old) in the Paigalabadda District of the Kalutara Totamune which have been tapped year after year and which would be blown down if not supported by the couplings, yield best. They are very scraggy looking but they are commonly known as 'toddy trunks'."

It is quite usual to tap two spathe on a tree. The average time which is taken to use up a spathe, i.e., to pare it away, varies in different places from 30 to 90 days, much depending upon the care with which the tapper prepares it each day. If the spathe is one giving a good yield, a Cochin tapper will only shave off a very thin portion each time he taps. It is in his interest to get the maximum yield from each tree since he is

paid by the number of gallons he draws each day. The total yield per spathe varies from 3½ to 17½ gallons, i.e., from about 15 to about 75 litres.

Trees which are being tapped do not give a good yield of nuts on the other spathes.

#### Uses and processes of treatment.

Coconut toddy, drawn as described in the previous section, is used for three main purposes, namely, for the production of crude sugar, as a beverage, and for the distillation of a potable spirit. It is also used to a small extent for the production of vinegar.

For use as a sugar basis, the toddy must be drawn unfermented. The inhibition of fermentation is usually attained by placing a small amount of slaked lime in the collecting pots each day, when they are put on the trees. This is the present official regulation with regard to the collection of sweet or unfermented toddy.

It was believed until quite recently that the bark and leaves of certain plants, if placed in the collecting pots, would prevent fermentation. These plants were *Valeria acuminata* (Sinhalese, "Hal"), *Cymnosome pedunculata* (Sinhalese, "Ankenda"), and *Garcinia cambogia* (Sinhalese, "Goraka"). It was found by us on investigation that none of these was in any way effectual in preventing fermentation. Hal bark is however useful for clearing toddy which is to be made into jaggery (crude sugar), this action being presumably due to the presence of tannins in the bark. If an absolutely new unused pot is used for collecting the toddy, the liquid remains practically unfermented for a considerable time, possibly in part on account of salts dissolved out from the unused pot. Tappers say that a new pot must be used without cleaning for six days before the normal results are produced, i.e., before the toddy when collected is vigorously fermenting. In an old pot there is always a considerable accumulation of wild yeasts and bacteria on the inside. Hence fermentation is rapid, since the sugary liquid enters drop by drop into a strong culture of yeasts. On one occasion when we wished to collect normal toddy from a particular tope the owner was warned beforehand of our visit. In order presumably to please us he had everything cleaned up, even the toddy pots. Hence the toddy which we collected that morning was anything but normal, being practically unfermented.

If drawn in a glass pot, which is clean and practically sterile, toddy likewise remains unfermented.

Apart from the above-mentioned "lining" of the pots for sweet toddy, the process of tapping and collecting is carried out in the same way as for ordinary or fermented toddy, but in every case the yield of juice is very much smaller. This difference of yield is unmistakable. It is difficult to assign any particular reason for this.

The actual process of manufacture of the crude sugar (jaggery) from the sweet toddy is very primitive and is practically all carried out by small native proprietors.

The collected toddy, containing lime as stated above, is first strained to get rid of insects, etc., which swarm into the toddy pots; it is then boiled down in large earthenware pots over wood or coconut husk fires until it is of a syrupy consistency. When of the proper consistency, as ascertained by trial, it is poured into empty coconut shells and allowed to solidify. The resulting product varies considerably in colour, from nearly white to dark brown. It is usually very deliquescent.

Approximately 1½ lb. of jaggery can be manufactured from one gallon of toddy. Locally this crude sugar is used as a substitute for imported sugar and for the preparation of sweetmeats. Its taste is quite characteristic. This industry in

jaggery appears to have been of considerable importance in the past, since, according to Bertolacci, the value of jaggery exported from Ceylon in the year 1813 was 39,425 rix-dollars (£2628). Since the introduction of cheap imported sugar and the increasing demand for copra for the manufacture of coconut oil, the industry appears to have died down, as there is no record of any export of jaggery for the last few years. At the present time the chief source of jaggery for local consumption is Kital or Palmyrah toddy.

As a beverage, toddy from the various kinds of palms before mentioned, i.e., coconut, kital, and palmyrah, is in very considerable demand in most parts of the island. The toddy as drawn from the trees (in unlined pots) is brought in the morning (and in some cases also in the evening) to the taverns where it is sold by retail. As will be seen from the next section, it varies very considerably in composition, but this is only natural since its fermentation, etc., is entrusted to any chance yeasts and bacteria which may make their way into the collecting pot on the tree. For the same reason this toddy must be treated as a perishable product (like milk) and cannot be stored under present conditions. To most Europeans its smell is repulsive; but when once this is overcome, fresh fermented toddy becomes quite acceptable as a refreshing drink. Though not clear, it is strongly sparkling, as it is still fermenting when consumed. In appearance it somewhat resembles very dilute milk. Its taste may be compared with cider in harshness, with at times a suggestion of a flavour resembling champagne. It thus forms a good local substitute for beer. It should also be a very healthy drink, since it contains a large percentage of yeast; in fact it may be said to be a suspension of yeast in a liquid containing a certain amount of alcohol, sugar, and acid. However, it rapidly sours, and the morning's toddy is not pleasant to drink in the evening, except in cool weather or in the cooler parts of the island where the acid production is not so rapid. After 24 hours the liquid is too acid to drink.

Toddy is used as a food and drink combined by some of the fishermen along the coast, who start their day's work with only the fortification of a drink of toddy to sustain them. For the production of a potable spirit, arrack, a very considerable amount of coconut toddy is used in Ceylon. The process is almost entirely carried out in very primitive copper pot stills, heated by wood fires. Condensation is effected by means of a copper worm in a vat of water. This water is not circulated during distillation and no rectifiers are used. The resulting spirit is, as may be imagined, of a very inferior quality and is very seriously contaminated with copper, etc. The distilleries number rather over 250, and are practically all situated near the coast on the south-west of the island. In this distillery area most of the toddy is reserved for distillation.

The toddy is collected at the topes (gardens) in barrels which are either carted to the distilleries or rolled along the roads thither. As most of the stills are very small, it might have been thought that sufficient toddy would be brought in each day to fill the still (100–200 gallons) and that it would be distilled as soon as possible, as fermentation is practically complete by the time the toddy reaches the distillery. This, however, is not the custom. It is usual to keep the toddy in open vats in the distillery for three or four days, by which time it has become very acid and much of the alcohol has become lost. As a result, the yield is poor and the product is bad. The condensing worm becomes coated with an acid greasy deposit which attacks the copper. The mere advice of a scientific visitor has, however, no effect in altering the custom of years, and the same wasteful process will possibly go on indefinitely.



The spent wash from the stills is usually run out on to the ground outside the distillery wall and serves as a food and as a wallowing ground for cattle and pigs, with a resulting smell which must be experienced to be properly appreciated. The total amount of arrack distilled in the

Alcohol was estimated by the usual distillation, followed by a density determination.

The actual observations made amounted to several thousands, and the following table gives characteristic readings taken on unfermented, slightly fermented, and fermented toddy.

	Sp.gr.	@ F.	K.	R. <sub>50</sub>	Total solids, grms. per 100 c.c.	Ash, grms. per 100 c.c.	Sucrose, %	Acidity (less CO <sub>2</sub> ), %	Proteins, %	Alcohol, % by weight.	
1. Unfermented	1-058	86°	4900	67-9	15-19	0-33	13-5	0-145	0-32	—	Collected in a sterile glass vessel.
2. Slightly fermented...	1-077	86°	5100	—	17-22	0-398	10-0	—	0-23	—	
3. Unfermented	1-063	80°	4500	71-8	16-22	0-156	12-3	—	0-20	—	
4. Unfermented	1-060	84°	4100	70-0	15-82	0-31	13-75	0-21	0-25	—	Collected in a sterile earthenware pot. Collected in a sterile glass vessel. Ditto. Ditto.
5. Unfermented	1-060	84°	4000	70-0	16-18	0-31	12-9	—	—	—	
6. Unfermented	1-061	84-5°	4000	72-5	16-28	0-31	12-0	—	—	—	
7. Unfermented	1-067	85°	4600	81-0	19-6	0-33	17-4	—	—	—	
8. Unfermented	1-065	85°	4700	—	17-0	0-39	—	0-005	—	—	
9. Unfermented	1-066	84°	5300	77-7	17-39	0-41	—	0-05	—	—	
10. Unfermented	1-067	84°	4900	78-9	19-03	0-11	17-4	Nil	—	—	
11. Fermented...	1-001	83°	5300	—	2-43	0-33	—	0-35	—	5-8	
12. Fermented...	1-005	85°	5000	—	3-36	0-23	—	0-32	—	4-9	

Island is approximately 1½ million gallons of 25° u.p. per annum. Practically all this is consumed locally, only a few thousand gallons being exported. As in the case of jaggery, this export of arrack has dropped very much from what it was in the past when Ceylon arrack was much in favour in India. Bertolacci records that in the year 1810 the export of arrack amounted to 980,700 gallons, whereas the total export for the financial year 1909-1910 was only 4612 gallons.

For the production of vinegar, toddy is allowed to become sour and is then stored in partially open vats with certain herbs for a considerable time, up to one year. The resulting vinegar is of fair quality, and may have an acidity of as much as 6% reckoned as acetic acid.

#### Analytical details.

The conductivity (K) was estimated on an Evershed and Vignoles Dionic water tester.

This consists essentially of a glass tube with two electrodes. The electrodes are connected to a direct reading conductivity meter and a continuous current hand-driven dynamo. One unit of conductivity is the reciprocal of a megohm. The ordinary scale only extends to 2000 units, so the makers introduced a switch, in the meter, which can raise the scale reading to 20,000 units. Readings were taken at 30° C. It was found as the result of a large number of fermentations with different yeasts that the conductivity was unchanged as fermentation proceeded.

The refractive power (R<sub>50</sub>) was taken at 30° C. by a Zeiss immersion refractometer.

The total solids were estimated by drying at 100° C., the final drying being done *in vacuo* at 50° C.

The ash was estimated as usual in a Hoskins electrically heated muffle.

The sucrose was estimated by a large Hilger polarimeter. It was found that the best way to get a clear solution was to use the minimum quantity of a crystalline basic lead acetate (usually 1 gram per 100 c.c. of toddy) followed by centrifuging, precipitating the lead by dry potassium oxalate, and re-centrifuging. It is very difficult to get a clear solution. For proteins, the factor N × 6.37 was used.

The acidity after boiling off CO<sub>2</sub> under a reflux condenser was estimated by standard baryta and phenolphthalein, and was calculated as acetic acid.

The changes as fermentation proceeds were followed by adding, to sterile toddy, small quantities of yeasts separated from fermenting toddy by centrifuging. The following is a typical example:—

At start.	4 hours later.	24 hours later.	In 27½ hours.	In 48 hours.
Sp.gr. at 85° F. 1-071	1-055	1-013	1-007	—
Alcohol. Nil	1-2% by weight.	5-85	5-85	6-6%
Acidity (less CO <sub>2</sub> )	0-16%	0-23%	0-33%	0-43%

A sample of toddy containing 17% sucrose had R<sub>50</sub> = 79.3 and specific gravity 1.069 at 85° F. In 24 hours the figures were sp.gr. 1.020 at 85° F., refraction 46, alcohol 5.6% by weight; 5½ hours later the figures were sp.gr. 1.010 at 85° F., refraction 40, alcohol 6.6% by weight. Polarimeter readings showed invert sugar equivalent to a little over 1% sucrose. In 50 hours after fermentation had started the figures were: sp.gr. 1.001 at 84° F., refraction 33, alcohol 6.45% by weight. Polarimeter readings showed no sugar left.

A sample having sucrose, 17.4%; sp.gr. 1.067 at 28° C.; conductivity 4900 units; refraction, 78.9 at 30° C.; total solids, 19.68 grms. per 100 c.c.; ash, 0.107%, and faintly alkaline to phenolphthalein was mixed with freshly separated toddy yeasts. On July 23rd at 12 a.m. the mixture had a sp.gr. 1.067 at 28° C. and refraction 78.5 at 30° C. At 11 a.m. on July 24th the sp.gr. was 1.033 at 28° C., refraction 53, acidity (less CO<sub>2</sub>) 0.06% acetic acid, and alcohol 4.8% by weight. At 4 p.m. on July 24th, the sp.gr. was 1.020 at 28° C., refraction 46, acidity (less CO<sub>2</sub>) 0.08% acetic acid, alcohol 5.3% by weight. At 11.30 a.m. on July 25th, sp.gr. 1.002, refraction 34, acidity (less CO<sub>2</sub>) 0.16% acetic acid, alcohol 7.4%. At 4 p.m., July 25th, sp.gr. 1.000, refraction 32, alcohol 7.65%, acidity 0.18% acetic acid. Polarimeter readings showed that all the sugar left (just over 1%) was inverted.

The percentage of alcohol in fermented toddy just prior to distillation varies in an astonishing fashion owing to the crude fermentation methods used. In one distillery, for example, 22 samples, taken throughout the season, showed an alcohol content varying from 8.8% to 2.6% by weight, the average being about 4%.



The electrical conductivity was usually between 4000 and 5000 units. After heavy rain, the conductivity falls, owing to water getting into the pots, and has been found as low as 2750 units.

The acidity (less  $\text{CO}_2$ ) calculated as acetic acid was usually under 1%. If the toddy is kept the acidity rises rapidly and with samples a month old acidities of over 6% acetic acid have been found.

*Sugar.* Up to the present only sucrose (and of course dextrose and levulose) has been definitely found in the toddies examined. It is possible, however, that some contain a little raffinose.

As a rule one particular source of toddy gives a fairly constant yield of sugar. For example, 55 samples taken from one district in August and September showed a variation in specific gravity of 1.060—1.068, the sucrose varying from 15% to 18.4%, the mean being 1.064 with an average yield of 16.9% sugar. In conclusion the average percentage of sucrose in unfermented toddy is high and fairly constant and an important industry could be developed by making crystalline sugar and fermenting the molasses left, by suitable ferments, for alcohol. The present methods are crude in the extreme, and not only produce a very bad quality spirit but are wasteful, losses of over 50% of the available sugar being common.

A considerable number of samples of toddy have been examined in various parts of the Island as sold over the counter in toddy taverns and also in the topes where tapping was taking place. The following figures give the results for 50 samples of coconut toddy.

Specific gravity, average 1.012, varying from 0.998 to 1.033. Acidity averages 0.51%, varying from 0.32% to 0.67% reckoned as acetic acid.

Alcohol, by weight, averages 4.2%, varying from 2.7% to 5.8%.

As is to be expected there were very considerable variations in acidity and alcohol percentage, due to various soils, or the state of fermentation of the juice.

Gibbs (*loc. cit.*) gives the following figures for Philippine coconut toddy. The average daily yield of sap is 650 c.c. and a good tree will give about 500 litres a year. The average composition of fresh sap is: Density 1.070, total solids 17.5%, acidity trace, ash 0.40%, sucrose 16.5%, invert sugar, trace. Undetermined nitrogenous compound 0.60%.

#### *Organisms present in fermented toddy.*

A number of samples of toddy were sent to Copenhagen for examination by one of the authors in the Alfred Jørgensen Laboratory. The specimens were sent on plugs of cotton wool in sterilised test tubes. On receipt the samples were placed in suitable media, and after a short delay growths appeared which were examined in detail. In most cases pure cultures were made, i.e., cultures grown each from a single cell.

*Yeasts.* The yeasts thus isolated consisted of the following types:—

(a) *Saccharomyces cerevisia*, or some very nearly allied yeasts.

This resembled a typical culture yeast. Several strains of this yeast were isolated in pure culture and showed normal phenomena of sporulation and budding, with top fermentation.

(b) A wild *Saccharomyces*, resembling a wine yeast.

This was a typical "wild" yeast, somewhat resembling *S. ellipsoideus*, with rather large but otherwise typical highly refractile spores, in shape resembling oblate spheroids. Fermentation with this yeast was fairly rapid and very complete in a solution containing 16% of sucrose.

(c) *Schizo-saccharomyces*, or fission yeasts.

These were all typical fission forms, resembling *Schizo-saccharomyces mellacet*. Fermentation with these yeasts was rather slow in starting but gave a good yield.

(d) *Zygo-saccharomyces*, or fusion yeasts.

Somewhat resembling in phenomena *Z. Barkeri*, but of no interest from the fermentation point of view.

(e) A *Saccharomycode* form, resembling *S. Ludwigii*.

No species of film-forming yeast or mycoderma or torula was found.

*Moulds.* The species of these forms which were present in a living state in the samples of toddy belonged almost entirely to the class of moulds which most closely resemble yeasts such as *Monilia* and *Oidium*. In the media available in the laboratory the specimens gave no signs of fructification, propagation showing itself only under the forms of budding and fission.

*Bacteria.* Many bacteria were found in the samples and any sample of toddy is always characterised by the presence of many long chains of these organisms.

It is not thought necessary to enter into any detail with regard to the organisms present in toddy, since firstly it is most probable that a sample of fresh toddy will be found to contain many more varieties than those which survived the journey to Europe, and secondly it is hoped that it will be possible at some future date to make a complete examination, and publish the results in a separate paper.

## RUBBER VULCANISATION TESTS.

BY H. P. STEVENS, M.A., F.L.C.

The paper by Eaton and Grantham in the October 31st issue of the Journal (pp. 1046—1050) appears to be a reply to the point raised (this J., 1916, 501) as to the exclusive use by these authors of a mixing composed of 90% rubber and 10% sulphur, and the assumption that what applied to such a mixing applied in the same manner and degree to other mixings. The tenor of their reply is that it applies in the same manner but not to the same degree.

In their various papers Eaton and Grantham give rates of cure at 140° C. for plantation Para rubber varying from about one to four hours and I certainly had the impression that they supposed that similar variations take place in the rubber factory. For instance they write "It is only necessary to see the vulcanised specimens [their own] which have been prepared to realise the manufacturer's dilemma, etc," or again "the variability in respect of rate of cure which was shown to be the most important variation in different raw rubbers, both from the manufacturer's standpoint, etc." As no tests had been made except with a "theoretical mixing," that is, one not used or barely if ever used in a rubber factory, the statements made are not justified unless one assumes that the rubber mixings commonly employed in the factory show the same degree of variation in rate of cure as the theoretical mixing actually used.

So far, however, from differing from Eaton and Grantham, I am in general agreement with them as to the effect of introducing mineral matter or reducing the proportion of sulphur. The result is that, according to their own showing, the introduction of a few per cent. of litharge almost obliterates the difference in the rate of cure (as shown by their curves) between their fast and slow curing rubbers. These specimens were chosen to show as great a difference as possible in rate of cure, the difference being greater than that usually met with in commercial plantation Para rubbers (first latex). It would almost appear as if a manufacturer could substitute one such rubber by another without appreciable alteration in the rate of cure of this mixing. The importance of litharge as an ingredient of technical mixings cannot be overrated. Previous to the great

increase in the output of tyres, more rubber was consumed in the manufacture of rubber shoes (galoshes) than in any other branch, and these always contain litharge. No statistics are available but quite possibly more than half the rubber goods manufactured contain litharge, and that is why some manufacturers use a mixing containing litharge for testing purposes.

Eaton and Grantham attribute the effect of litharge entirely to its action as an accelerator, but if this explanation were sufficient, magnesia should produce a similar effect. Judging from the curves (compare 138 A and E with 138 B and F) the addition of magnesia to the compound containing zinc oxide does not appreciably reduce the difference in rate of cure between the fast and slow curing rubbers. The explanation may be found in recent work of my own (this Journal, 1915, p. 524).

The title of Eaton and Grantham's paper is somewhat misleading as their mixings can hardly be regarded as generally representative of technical work. The great bulk of these contain a larger number of mineral ingredients as well as "substitute," "reclaim," etc. Nevertheless the mixings chosen are in my opinion suitable as types for research work. Finally with reference to Eaton and Grantham's "optimum cure." The authors explain that if two rubbers be taken with "optimum" cures of  $3\frac{1}{2}$  and  $1\frac{1}{2}$  hours respectively and the former be found overcured by say  $\frac{1}{2}$  hour the correct cure of the latter may be deduced by subtracting  $\frac{1}{2}$  hour from the "optimum" cure, giving a correct cure of one hour. This method appears crude and no proof or explanation is given of so simple a relationship. It is easy to show that it cannot be accepted as correct. I have shown (this Journal, 1916, 872-874) that the "optimum cure" as determined by Eaton and Grantham may exceed the correct cure by an hour or more. If we subtract this amount from the cure of the second rubber we are left with a correct cure of  $\frac{1}{2}$  hour or less. It is therefore obvious that this simple arithmetical relationship cannot hold. If a simple relationship between the "optimum cure" and the correct cure be required *merely as a working hypothesis*, it would be better to adopt a geometrical relationship and to calculate the correct cure of the second sample by multiplying by the correct cure of the first and dividing by the "optimum cure" of the first. Thus if the "optimum" and correct cures of the first sample be  $3\frac{1}{2}$  and  $2\frac{1}{2}$  respectively we may calculate the correct cure of the faster curing rubber by the factor  $\frac{2\frac{1}{2}}{3\frac{1}{2}}$ , giving a provisional figure of 0.87 hour approximately.

#### JOINT HOUSING OF METALLURGICAL AND MINING SOCIETIES.

At a recent meeting of the Iron and Steel Institute, reference was made to the proposal to secure a joint building for the housing of our four great metallurgical and mining societies, namely, the Iron and Steel Institute, Institution of Mining Engineers, Institution of Mining and Metallurgy, and Institute of Metals. At present, three of these Societies have suites of rooms in Westminster, whilst the Institution of Mining and Metallurgy occupies its own premises in the City. A preliminary meeting of representatives of these Societies will be held shortly, and, if the main principles of the scheme can be agreed to, definite proposals will be submitted to the Councils of the respective Societies. It is not proposed that the Societies should sink their identity in an amalgamation of mining and metallurgical societies, as has been suggested recently by Prof. Armstrong for the chemical societies of the country; but it is realised that the centralisation of the 8000 members of the Societies in question, under a common

roof, with suitable meeting rooms and adequate library accommodation, would be to the advantage of all.

In this connection it is interesting to note the excellent results that have followed a similar joint housing scheme in America, where, since 1907, the American Institute of Electrical Engineers, the American Society of Mechanical Engineers, and the American Institute of Mining Engineers have occupied the splendid premises in West 39th Street, New York, known as the Engineering Societies' building. Quite recently the American Society of Civil Engineers has decided to join the other societies in the same building, and three further storeys are being added for their accommodation. When completed, the building will house institutions having a combined membership of 28,000, with a library containing 70,000 books and 90,000 pamphlets.

Another instance of the successful housing under one roof of societies having allied interests is to be found in the Chemists' Club, New York, where the American Chemical Society, the American Electrochemical Society, and the New York Section of the Society of Chemical Industry have met for some years past with the happiest results.

With these examples of successful co-operative effort before them, it is to be hoped that in the near future the societies which represent chemistry in all its phases in this country will take active steps to come together in a joint building, where a representative chemical library, for which there is a real need, could be established.

#### London Chamber of Commerce.

*Special Meeting of Chemical Section held on  
October 27th 1916.*

In reference to the above meeting, a report of which was printed in the last issue of this Journal (pp. 1093-1095), Mr. R. J. Pugh, of the London Chemical Works, Southall, writes that since the outbreak of war his firm has established an industry for the manufacture of salicylates, and is able to produce sufficient for the needs of this country and her Colonies; immediately after the war, however, Germany will despatch to this market salicylates at such prices as will make it impossible for the English manufacturer to compete, owing to the smallness of the British production, and the vastness of German chemical industry, which will enable them to sell articles here at less than cost price. Mr. Pugh therefore proposes that the Chemical Section of the London Chamber of Commerce should secure a powerful Committee to ascertain which of the chemical industries can produce sufficient of their particular product to at least meet the requirements of this country and her Colonies. The data thus collected would be placed before the proper authorities, to serve as a basis for some form of protection. The suggested form which this should take is that the import of particular chemicals from abroad should be prohibited until the respective industries have attained a position which will enable them to compete with the much larger businesses in Germany. The proposed Committee would have to guarantee on behalf of the manufacturers that the price charged for the article would not be more than sufficient to provide a reasonable profit.

Dealing with the expansion of trade with British Colonies after the war, Mr. Pugh suggests that the Chamber of Commerce might create a special Department to acquaint our manufacturers with the particular requirements of the various parts of the Empire, and at the same time provide the Colonies with particulars of British manufactures.

### Obituary.

#### DAVID HOWARD.

British chemical industry has sustained a great loss in the death of Mr. David Howard at the age of 78 years. Whilst travelling from his home at Buckhurst Hill to his Ilford factory on November 14th, he suddenly became insensible and expired a few minutes afterwards from heart failure.

The loss to this Society is an equally great one, for he had been one of its most loyal supporters since its foundation, and his record of service on its Council and committees is a remarkable one. He was elected a member of the first Council in 1882, and became a vice-president in 1883, serving in that capacity until 1885. He was elected President in 1886, and on retiring from the Presidency in 1887 he was again elected a Vice-President, serving until 1889, and again from 1890 to 1893, 1897 to 1900, and 1904 to 1907. He also sat on the Council as Ordinary member from 1894 to 1897 and from 1901 to 1904, and presided over the London Section of the Society as Chairman from 1883 to 1890. He was elected a member of the Publication Committee in January, 1883, and continued to serve in that capacity until his death; he was one of the most regular attendants at the meetings of that Committee, and his work and advice were greatly valued.

Born at Tottenham in 1839, David Howard was the son of Robert Howard and grandson of Luke Howard, F.R.S., who founded the great business at Stratford now known as Howards and Sons, which has acquired a world-wide reputation for its products, notably quinine, but also including many other "fine chemicals." His first association with the business was in 1857, and later he attended the Royal College of Chemistry as one of Hofmann's pupils. In 1860 he became a partner in the firm, and when it was formed into a company, in 1903, he was made chairman, with his two sons, David Lloyd Howard and Bernard F. Howard,

and his nephews, A. G. and G. E. Howard, as his co-directors. The business of the firm expanded to a remarkable degree whilst he had the control of its destinies, and some years ago the head-quarters had to be removed from Stratford to the large premises at Ilford which it now occupies.

David Howard was one of the greatest authorities on quinine and other cinchona alkaloids, and contributed several useful papers dealing with these substances to scientific Journals, his first communication being made to the Chemical Society in 1871.

The great interest which he took in the promotion of chemistry and chemical industry is evidenced from the fact that, in addition to his long connection with this Society, already referred to, he was Treasurer of the Institute of Chemistry from 1884 to 1903 and President from 1903 to 1906, also serving on its Council as well as on three separate occasions on the Council of the Chemical Society, of which he had been a member since 1869. He was also an enthusiastic supporter of the London Chamber of Commerce, and was for some years Chairman of the Chemical Trade Section. He took a very active part in the agitation for promoting moral rectitude in business transactions, which led up to the passing of the Prevention of Corruption Act, and later acted as Chairman of the Bribery and Secret Commissions Prevention League which was formed to carry into effect the provisions of the Act. He was also a Justice of the Peace for the Borough of West Ham and a Deputy-Lieutenant for the County of Essex.

The passing of David Howard leaves a void in the chemical life of this country which it will be impossible to fill. His sterling character, his remarkable personality, his wide learning, and his genial disposition will never be forgotten by those who came in contact with him, while those who had the advantage of his closer personal acquaintance feel that they have lost a very true friend.

## Journal and Patent Literature.

PATENT SPECIFICATIONS may be obtained by post by remitting as follows:—

English.—6d. each, to the Comptroller of the Patent Office, Southampton Buildings, Chancery Lane, London, W.C.

United States.—1s. each, to the Secretary of the Society, who has to furnish the U.S. Patent Office with the following data:—Patent number, date, name of patentee, and title of invention.

French.—1 fr. 05 c. each, as follows: Patents dated 1902 to 1907 inclusive, Belin et Cie., 56 Rue Feron 8, Paris (Se); Patents from 1908 to date, L'Imprimerie Nationale, 87, Rue Vieille du Temple, Paris.

### I.—GENERAL; PLANT; MACHINERY.

*Colloidal solutions; New method for the purification of*—G. Wegelin. *Kolloid Zeits.*, 1916, 18, 225—237. *J. Chem. Soc.*, 1916, 110, ii., 520—521.

The method depends on ultra-filtration by the use of a collodion membrane. The apparatus consists of a funnel-shaped vessel containing the colloidal solution to be purified, this vessel being closed near the top by the ultra-filter, whilst water under pressure may be introduced through the lower narrow end of the funnel, the rate of flow being regulated by means of a tap. The aqueous solution which passes through the collodion filter is run off into collecting vessels. It is essential that the flow of liquid should be upwards, for preliminary experiments in which the colloidal solution was placed above the ultra-filter showed that the colloidal particles, under the continued influence of gravity and of the current of liquid,

tended to accumulate on the upper surface of the membrane to such an extent that this rapidly became impermeable to the wash water. For the production of suitable filters, the author recommends the use of solutions of nitrocellulose in acetic acid. The solution, of from 7.5 to 15% strength, is spread out in a uniform, thin layer on a glass plate, and the film subjected to the action of running water for five to ten minutes. The porosity varies very considerably with the concentration of the collodion, a membrane prepared from a 7.5% solution having been found to be about ten times as porous as that prepared from a 15% solution. The membranes may not be dried, and even when kept under water it is found that aging takes place. The apparatus has been found to give satisfactory results in the purification of colloidal solutions of antimony, arsenic, and molybdenum sulphides; gold, palladium, silicic acid, ferric hydroxide, aluminium hydroxide,

vanadium pentoxide, blood serum, and egg-albumin. The apparatus may also be employed for the preparation of colloidal solutions containing particles of determinate size, for the concentration of dilute solutions of colloids, for measurements of the size of colloidal particles, and for the purification of precipitated substances which cannot be easily washed by the usual filtration methods.

## PATENTS.

*Heating, cooling, condensing, and cleaning or purifying fluids, and the like; Tubular apparatus for —.* O. J. Goodwin, and O. Guttmann and Sons, London. Eng. Pat. 14,165, Oct. 6, 1915.

STRIPS of metal twisted into helical form are inserted in the inlet end of a tube through which fluid circulates, the pitch of the helix decreasing in the direction of flow.—W. F. F.

*Cooling towers.* F. Uhde, Breslau, Germany. Eng. Pat. 14,492, Oct. 13, 1915. Under Int. Conv., Feb. 25, 1915.

WATER to be cooled enters a series of horizontal troughs at the top of the tower, and overflows over cooling hurdles to similar troughs at the bottom, from which it is discharged at the centre into a conical collecting vessel. This vessel extends upwards from the ground level nearly to the lowest trough so that a head of water is maintained on the suction side of the circulating pump to decrease the power used. Air enters the bottom of the tower around the periphery and passes upwards over the hurdles.—W. F. F.

*Cooling vapours or gases issuing from condensers; Apparatus for —.* F. Fahl, Bremen. Ger. Pat. 293,896, Nov. 13, 1913.

A RECEPTACLE containing a cooling liquid is arranged above a horizontal condenser and is divided into compartments by partitions projecting alternately from the top and bottom. The gases or vapours leaving the condenser enter the receptacle at one end and pass successively through the compartments, displacing the cooling liquid therein. The first compartment contains a float, and as the liquid level falls, the float actuates a valve, and a fresh supply of cooling liquid is delivered to the receptacle.—A. S.

*Compressed gases and the like; Apparatus for use with —.* L. B. Hall, Winchmore Hill, Middlesex. Eng. Pat. 11,535, Oct. 14, 1915.

THE compressed gases are released from the vessel in which they are stored, by a revolving telescopic key, fitted with a back-pressure valve. Leaks at the joints are prevented by the use of an external flexible sleeve.—W. H. C.

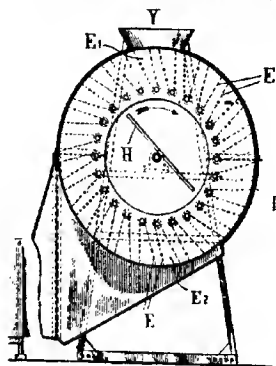
*Dryer.* F. Koblenz, Brackwede. Ger. Pat. 293,416, May 27, 1914.

THE material to be dried is contained in a series of horizontal cylinders or drums mounted on a pair of endless chains. The drums are carried through a heated chamber by the chains and are simultaneously rotated. One end of each drum is formed by a set of wings or blades, which act as a fan and force a current of hot air through the material in the drum.—A. S.

*Drying substances; Process and apparatus for —.* G. H. and J. H. Stroband, Amsterdam. Eng. Pat. 100,403, Apr. 28, 1916. Under Int. Conv., May 1, 1915. (Appl. No. 6117 of 1916.)

AIR is passed in a continuous stream through a chamber containing calcium chloride and then through a heater to a rotating or oscillating drum. The air enters through openings in the bottom,

traverses the material to be dried, and escapes at the outlet, Y. Prisms of wire gauze or webbing, E, are provided to distribute the air, and a perforated



plate, H, agitates the material. Opposite prisms, E, E1, may be removed for charging and discharging. The apparatus is suitable for drying grain, fruits, casein, chemicals, etc.—W. F. F.

*Crystallisation; Apparatus for continuous —.* Norsk Hydro-Elektrisk Kvaestofaktieselskab. Fr. Pat. 479,668, Sept. 4, 1915. Under Int. Conv., Sept. 17, 1914.

THE solution is fed into the upper end of a rotating cylinder which is inclined at a very slight angle to the horizontal. Water is sprayed on to the outside of the cylinder, and a fixed scraper is provided inside to lift up the crystals as the cylinder rotates. The crystals and mother liquor are discharged from the open lower end of the cylinder into a shoot, which guides them to centrifugals or other drying apparatus.—W. H. C.

*Desiccation of gases intended to be liquefied.* J. Cartier. Fr. Pat. 479,749, Sept. 15, 1915.

THE gas is mixed with a small proportion of the previously liquefied gas and the fall of temperature, due to the expansion of the latter, causes the deposition of the moisture in the gas. The gas is subsequently passed through a scrubber filled with coke or other suitable material to retain the deposited moisture.—W. H. C.

*Liquefying gases with low boiling point; Apparatus and process for —.* G. Hildebrandt, Spandau-Tiefwerder, Germany, Assignor to American Industrial Gas Co., New York. U.S. Pats. 1,199,700 and 1,199,701, Sept. 26, 1916. Dates of appl., Jan. 9, 1911, and June 11, 1914.

SEE Eng. Pat. 3316 of 1910; this J., 1910, 1446.

*Evaporating, etc.; Method of —.* O. Söderlund and T. Boberg, Assignors to Techno-Chemical Laboratories, Ltd., London. U.S. Pat. 1,300,996, Oct. 10, 1916. Date of appl., Oct. 14, 1912.

SEE Eng. Pat. 22,670 of 1911; this J., 1913, 183.

## IIA.—FUEL; GAS; MINERAL OILS AND WAXES.

*Hydrocarbons contained in coal; Some —.* A. Pictet, L. Ramseyer, and O. Kaiser. Comptes rend., 1916, 163, 358–361.

LARGE-SCALE experiments on the extraction of coal with boiling benzene (this J., 1915, 163) furnished 0.25% of a product from which a liquid with the characters of "vacuum tar" (this J.,

1913, 1098; 1914, 70; 1915, 604) was separated. From this liquid the following hydrocarbons were isolated:—*Unsaturated*:  $C_7H_{10}$  (dihydrotoluene), b.pt.  $108^{\circ}$ – $110^{\circ}$  C.;  $C_8H_{12}$  (dihydro-*m*-xylene), b.pt.  $135^{\circ}$ – $137^{\circ}$ ;  $C_9H_{14}$  (dihydromesitylene), b.pt.  $166^{\circ}$ – $168^{\circ}$ ;  $C_{10}H_{16}$  (dihydronaphthalene?), b.pt.  $180^{\circ}$ – $182^{\circ}$ ;  $C_{11}H_{18}$ , b.pt.  $200^{\circ}$ – $202^{\circ}$ ;  $C_{12}H_{20}$ , b.pt.  $236^{\circ}$ – $238^{\circ}$ ;  $C_{13}H_{22}$  (dihydrofluorene?), b.pt.  $251^{\circ}$ – $254^{\circ}$ , m.pt.  $109^{\circ}$  C. *Saturated*:  $C_6H_{14}$  (?), b.pt.  $118^{\circ}$ – $122^{\circ}$ ;  $C_9H_{20}$  (?), b.pt.  $135^{\circ}$ – $138^{\circ}$ ;  $C_{10}H_{22}$  (?), b.pt.  $172^{\circ}$ – $174^{\circ}$ ;  $C_{11}H_{24}$ , b.pt.  $190^{\circ}$ – $192^{\circ}$ ;  $C_{12}H_{26}$ , b.pt.  $215^{\circ}$ – $216^{\circ}$ ;  $C_{13}H_{28}$ , b.pt.  $227^{\circ}$ – $229^{\circ}$ ;  $C_{20}H_{42}$  (melene), b.pt. above  $300^{\circ}$ , m.pt.  $62^{\circ}$ – $63^{\circ}$  C.

Some of the above hydrocarbons are present also in vacuum tar and in that case, therefore, must be regarded as derived from the coal by simple volatilisation. This leads to the view that coal is a solid hydrocarbon material impregnated with a liquid which is closely allied to petroleum. The extract obtained was feebly levorotatory ( $[\alpha]_D^{25} = -0.08^{\circ}$ ) and became dextrorotatory ( $[\alpha]_D^{25} = +0.27^{\circ}$ ) after eliminating alcohols, whereas optically active fractions have not been found in vacuum tar; it is suggested, however, that the active volatile constituents of the coal are racemised at the temperature of distillation.—F. SODN.

*Benzol recovery and rectification.* P. D. Walmsley and H. A. Morley. Manchester District Inst. Gas Eng., Oct. 28, 1916. J. Gas Lighting, 1916, 136, 229–234.

THE authors estimate that the present production of benzol is about 38 million gallons per annum and that if all the benzol was recovered from the coal carbonised at gas works, the production would be approximately 60 million gallons per annum. The oil used for absorbing benzol is generally coal tar creosote, but both anthracene oil and blast-furnace creosote are also used. The oil should be as free as possible from naphthalene and water, and the gas should be completely freed from ammonia before entering the benzol absorbing plant. Approximately 100 gallons of absorbing oil must be passed through the scrubbers for every ton of coal. The benzolised creosote oil leaving the scrubbers contains about 3% of benzol and this is recovered by distillation, either by direct fire or by steam, as "65% benzol," i.e., benzol which yields 65% of distillate at  $120^{\circ}$  C., when distilled in a retort, the bulb of the thermometer being immersed in the liquid. Steam is preferable where large quantities of oil are to be dealt with, and in a recent test 66 lb. of steam at 100 lb. per sq. in. pressure was required for every 100 gallons of benzolised creosote. The 65% benzol is rectified in the usual way after washing to remove impurities.—W. H. C.

*Tar from gas-producers using lignite as fuel; Utilisation of the —.* F. Fischer and W. Schneider. Stahl u. Eisen, 1916, 36, 549–554. Braunkohle, 1916, 15, 141–146. Z. angew. Chem., 1916, 29, Ref., 431.

THE tar is difficult to treat by the usual distillation processes owing to its high water content. By mixing 1 part of the tar with  $1\frac{1}{2}$  parts of powdered lignite, a stiff pasty mass is obtained which can be formed into rods. The rods are cut in pieces and then distilled, yielding 36% of crude oil and a dark grey, crumbly residue having a heating value of about 7000 cal. The tar may also be treated by extraction with petroleum spirit, either directly or after making into briquettes with lignite powder as described above. In this way about 40% of a brown grease can be isolated which can be used as a substitute for animal oils in the leather industry. From the residue about 20% of resinous matter can be extracted with benzene. The grease

extracted by petroleum spirit can be decolorised and deodorised by treatment with ozone in presence of sodium carbonate solution.—A. S.

*Naphthalene wash oils; New method of testing —.* J. Wohl. Z. Ver. Gas- u. Wasserfachm., 1916, 56, 132–135. Z. angew. Chem., 1916, 29, Ref., 426.

PROGRESSIVELY increasing quantities of naphthalene are dissolved in the oil, and a current of air is then drawn through the oil at the rate of 10 litres per hour, and after passing through a cooled washing bottle containing glass wool, is led into a solution of picric acid. After the limit of saturation of the oil under the experimental conditions is attained, some naphthalene vapour passes over with the air and is detected by the formation of a precipitate of naphthalene picrate.—A. S.

*Natural gas industry in the United States in 1915.* U.S. Geological Survey.

THE total quantity of natural gas produced in the United States in 1915 was 628,578,842,000 cu. ft., valued at \$101,312,381. This represents an increase of nearly 37,000,000,000 cu. ft. over the production of 1914, which was the largest hitherto recorded; the increase of value compared with 1914 amounted to \$7,196,857. The increased production was due chiefly to Ohio, Oklahoma, West Virginia, Pennsylvania, Kansas, and California, in the order given. Of the total quantity of gas produced, 65% (411,375,899,000 cu. ft.) was used for industrial purposes, at an average price of 9.7 cents per 1000 cu. ft., and 35% (217,202,943,000 cu. ft.) for domestic purposes, at an average price of 28.32 cents per 1000 cu. ft.

*Gasoline; Production of casing-head — in the United States in 1915.* U.S. Geological Survey.

THE quantity of gasoline extracted from natural gas in the United States in 1915 amounted to 65,364,605 U.S. gallons, valued at \$5,150,823, a gain of 22,712,033 gallons and \$2,044,914 over the figures for 1914. The quantity of natural gas treated, in 1915, was over 24,000,000,000 cu. ft., the average recovery of gasoline being 2.57 gallons per 1000 cu. ft. The number of plants increased from 386 to 414, and the total daily capacity of the plants from 179,353 to 232,336 gallons of gasoline.

*Cracked oil produced from petroleum; Recracking of a —.* G. Egloff and T. J. Twomey. J. Phys. Chem., 1916, 20, 597–620.

THE oils used for the experiments were: (1) a distillate or gas oil from Pennsylvania crude petroleum, and (2) a distillate boiling between  $170^{\circ}$  and  $360^{\circ}$  C. from the recovered oil produced by cracking (1). In each case the oils were cracked at atmospheric and 150 lb. pressure at temperatures of  $550^{\circ}$ ,  $600^{\circ}$ ,  $650^{\circ}$ , and  $700^{\circ}$  C., under identical conditions. At all temperatures and pressures the amount of oil recovered from the cracked oil was greater than that from the petroleum oil, showing that the former was not so well adapted for the production of gasoline or aromatic hydrocarbons. The amounts of benzene, toluene, and xylenes in the oil recovered from the petroleum oil were almost uniformly twice as large as those in the oil from the cracked oil, but apparently more naphthalene and anthracene were formed from the latter. Pressure increased the formation of aromatic hydrocarbons. For example, the following results were obtained from the petroleum oil at  $650^{\circ}$  C. at atmospheric and at 150 lb. pressure respectively:—Benzene, 5.0 and 24.5%; toluene, 7.0 and 10.3%; xylenes, 3.2 and 4.6%; and naphthalene 0.0 and 9.2%. Whatever cracking to hydrocarbons of lower boiling point takes place in a cracked oil must be attributed, in the main,

to the unchanged petroleum in the cracked oil. It is possible that gasoline may be obtained by a second cracking of an oil, but there is a limit to the process, since the tendency of the reaction is to produce aromatic compounds, which break up into carbon and hydrogen, rather than decompose into gasoline or benzene hydrocarbons.—C. A. M.

*The Messerschmüll process for the production of hydrogen.* Barnitz. See page 1137.

## PATENTS.

*Artificial fuel.* G. B. Winter, London. Eng. Pat. 101,609, June 29, 1916. (Appl. No. 9162 of 1916.)

BUNDLES of folded and rolled paper are tied with wire and immersed in paraffin wax at 140° C. for about 10–15 minutes.—W. F. F.

[*Regenerators.*] *Supply of air for combustion in the heating of gas retorts.* A. Waddell, Dunfermline. Eng. Pat. 14,143, Oct. 6, 1915.

A REGENERATOR is formed of vertical tubes of polygonal section arranged in a flue so as to provide tortuous passages between them for the hot gases or for the air to be heated. The lower ends of the tubes are secured with plastic jointing material in sockets in a tube-plate, and sand or other dry material is run through perforations in the upper tube-plate to complete the joints. The upper joints may be formed by means of asbestos rope or the like.—W. F. F.

*Waste heat of gas-retort furnaces; Utilisation of the* — F. Meddelmann und Sohn, Strassburg. Ger. Pat. 293,910, July 4, 1915.

A SECTION of the flue through which the hot gases from the furnace pass, is made to branch into two channels, the entrances to which are controlled by dampers. A boiler is placed in one of the channels, and the dampers are connected through an electro-magnetic circuit with a device sensitive to heat, placed at the point where the two branches unite again; the dampers are adjusted automatically so that the hot gases can pass through the channel containing the boiler only when a certain temperature is exceeded. The steam-outlet valve may be controlled simultaneously with the dampers.—A. S.

*Producer gas; Production of—* from heaps [of coal, etc.]. A. Riedel, Kössern. Ger. Pat. 293,430, Aug. 29, 1915.

PARALLEL perforated pipes are inserted in the heap at a suitable distance apart and serve to limit the portion of the heap to be treated at one time. Steam and air are introduced through one pipe, and producer gas is withdrawn through the other, but it is advantageous to reverse the flow of steam and air at intervals in order to prevent stoppages.—A. S.

*Gas producer, especially for power gas.* F. Kuers, Berlin-Tegel. Ger. Pat. 294,025, Mar. 28, 1915.

THE combustion zone at the bottom of the producer is connected with flues in the walls, which lead to an outlet flue controlled by a damper. A portion of the gas passes through these flues and serves to heat the descending fuel in the producer. In consequence of this it becomes possible to use a larger quantity of steam and to produce a mixture of water-gas and producer-gas more suitable than producer-gas alone for use in small gas-engines. The amount of gas escaping through the outlet flue is regulated according to the suction of the engine.—A. S.

*Gases (blast-furnace); Simultaneous purification, desiccation, and concentration of—* J. Weiwers. Fr. Pat. 478,260, July 23, 1914.

THE gas after a preliminary purification in ordinary

dust chambers is passed in succession through two towers where it meets finely divided streams of water, and through a vessel provided with a refrigerating coil by which the temperature of the gas is quickly reduced and the vapour, deposited first as a fog or mist and then as snow or frost, carries down the remaining dust particles with it.—W. H. C.

*Paraffin or crude or heavy oils; Method and means of using—* in internal combustion engines for motor cars, motor boats, aeroplanes, and other purposes. F. A. Wilkinson, Hatfield, Herts. Eng. Pat. 101,596, Apr. 25 and June 1, 1916. (Appl. Nos. 5921 and 7779 of 1915.)

PARAFFIN is sprayed and mixed with air in a carburettor of ordinary type, and hot exhaust gases are led by a small-bore pipe into the induction pipe of the engine to heat the mixture. An auxiliary air-admission valve is also provided on the induction pipe. To start the engine, the fuel may be heated by passing an electric current through a coil of wire in the float chamber of the carburettor, or in a separate chamber containing the fuel. The necessary fittings are adapted to be applied to an engine with a minimum of alteration.—W. F. F.

*Hydrocarbons; Apparatus for distilling—* G. F. Benhoff, jun., and J. O. Jensen, Baltimore, Md., U.S.A. Eng. Pat. 101,663, Apr. 7, 1916. (Appl. No. 5144 of 1916.)

VAPOUR from the still enters the lowest of a series of superposed cylindrical chambers forming a condensing column. Alternate chambers are spanned by vertical tubes through which the vapour passes and each set of tubes projects through the bottom of the chamber above, so as to trap condensed liquid which may be drawn off from each collecting chamber separately and, if desired, returned to the still. Air circulates round the tubes and through central passages in the collecting chambers.—W. F. F.

*Coke discharged from retorts or furnaces; Apparatus for removing—* Drakes, Ltd., and J. W. Drake, Halifax. Eng. Pat. 14,565, Oct. 15, 1915.

*Coke-oven; Regenerative—* E. Lecocq, Assignor to Soc. Gén. de Fours à Coke, Systèmes Lecocq, Brussels. U.S. Pat. 1,199,996, Oct. 3, 1916. Date of appl., Aug. 26, 1913.

SEE Fr. Pat. 460,399 of 1913; this J., 1914, 97.

*Gases; Apparatus for washing—* R. F. Pearce, Liverpool. U.S. Pat. 1,200,974, Oct. 10, 1916. Date of appl., June 3, 1916.

SEE Eng. Pat. 6199 of 1915; this J., 1916, 729.

*Production of a binding agent for tar-macadam roads.* Ger. Pat. 294,045. See IX.

*Manufacture of ultramarine.* Ger. Pat. 293,310. See XIII.

IIb.—DESTRUCTIVE DISTILLATION;  
HEATING; LIGHTING.

## PATENTS.

*Furnaces; [Reverberatory] heating—* R. F. and G. R. Hislop, Paisley, Renfrew. Eng. Pat. 5040, Oct. 1, 1915.

THE side walls of the fire-box of a furnace, of the reverberatory type, are supported upon a solid cast iron plate, with a flange on the under side of suitable dimensions to clear the sides of the ash-pan in the bottom, and of suitable depth to dip into the water in the pan, thereby forming a seal.



An air-box or receiver is contained in each of the side walls of the fire-box near the bottom, and is provided on the inside with openings for the tuyère pipes, with projections on the outside for cleaning or poking purposes, and with holes at each end for air and steam supplies respectively. Under the bed of the furnace, a round flue is constructed, extending to a point near the fire-box, and connected to the chimney at one end and the furnace bed at the other. One or more pipes, carrying the air to the air boxes, are placed spirally round the flue, so that the air is heated by the waste gases passing through the flue to the chimney.—B. N.

*Furnace; Gas-fired (heating)*——. C. F. Price, Birmingham. Eng. Pat. 14,668, Dec. 29, 1915.

The secondary air, after being heated by passing through a number of superposed passages arranged immediately below the combustion chamber, enters the latter by means of a series of longitudinal openings in the floor. The gas from the producer is introduced at one end of the combustion chamber.—W. H. C.

*Gas furnaces.* South Metropolitan Gas Co., and D. Chandler, London. Eng. Pat. 13,205, Dec. 31, 1915.

A GAS furnace consists of an annular burner tube with tangential mixing tube for gas and air, and burner nozzles projecting radial flames inwards. The burner nozzles are fitted with narrow slits deep enough to prevent lighting back. The furnace is particularly suitable for use as a "glory hole" for heating glass articles.—J. E. C.

*Furnace using oil or tar as fuel.* L. C. Strub, Zürich, Switzerland. Ger. Pat. 293,116, Feb. 28, 1916. Under Int. Conv., Nov. 3, 1914.

THE heating chamber is bounded at the bottom, back, and top by blocks of refractory material, in each of which are three flues, side by side. The middle flues serve for the introduction of the secondary air for combustion, and the outer flues for leading away the combustion products to the chimney. The oil or tar is supplied continuously to a dish placed on the floor of the heating chamber near the front.—A. S.

*Electric incandescence lamps with metallic incandescence body; Manufacture of*——. Deutsche Gasglühlicht A.-G., Berlin. Eng. Pat. 100,387, Feb. 23, 1916. (Appl. No. 2704 of 1916.) Under Int. Conv., May 4, 1915.

IN the manufacture of electric metallic filament lamps, metallic compounds such as barium azide ( $\text{BaN}_2$ ) are introduced. During the heating of the lamps, the metallic compounds are transformed by chemical decomposition into drying media (e.g., barium oxide) for the elimination of traces of moisture.—J. E. C.

*Electrical gas-lamp.* F. Skaupy, Assignor to Deutsche Gasglühlicht Akt.-Ges. (Auerger.), Berlin. U.S. Pat. 1,200,770, Oct. 10, 1916. Date of appl., May 12, 1914.

THE lamp is filled with a rare gas and is provided with a cathode consisting of an alloy of thallium and an alkali metal, having a melting point not higher than  $200^\circ\text{C}$ ., which is practically as soft as the alkali metal, but is more inert than the latter towards the material of the receptacle.—A. S.

*Process of producing creosote from hardwood-tar oils.* U.S. Pat. 1,199,271. See III.

*Manufacture of silicides of tungsten, molybdenum, zirconium, and other refractory metals.* Ger. Pat. 294,267. See VII.

### III.—TAR AND TAR PRODUCTS.

*Tar products; Effects of exposure on*——. C. S. Reeve and B. A. Anderton. Office of Public Roads and Rural Eng., U.S.A. J. Franklin Inst., 1916, 182, 463—475.

SEVEN samples of tar products, including two refined coal-tars, one refined water-gas tar, one refined mixed tar, two tar-asphalt mixtures, and one crude coke-oven tar, were subjected to the action of sun and air for three months, in a box designed to exclude dust. The authors give tables showing the percentage loss of weight each month, the figures at the end of three months varying from 3.87 to 24.24%. This loss of volatile products was accompanied by formation of "free carbon" (substances insoluble in carbon bisulphide). The tars hardened to a much greater extent than could be attributed to loss of volatile products alone, and tar products containing water-gas tar appeared to change to a greater extent than coal-tars. The comparative consistency of pitches from tars distilled to a single arbitrary temperature did not correspond with the behaviour of the tars in service.—J. E. C.

*Phenol in crude phenols from tar; Determination of*——. R. Masse and H. Leroux. *Comptes rend.*, 1916, 163, 361—363.

THE crude material (3 kilos.) is fractionally distilled from a 4-litre copper vessel fitted with a 60 cm. Vigreux column (this J., 1904, 1045), the rate of distillation being regulated to 7—8 c.c. per minute, and the distillate collected in 3 fractions: (a) below  $180^\circ\text{C}$ ., (b)  $180^\circ\text{—}203^\circ\text{C}$ ., and (c) above  $203^\circ\text{C}$ . (about 100 c.c.). Sufficient sodium chloride (35%) is added to fraction (a) to precipitate the dissolved phenol, which is added to (b), and the whole is transferred to a distilling vessel, utilising fraction (c) for rinsing purposes. With a column, as above, the liquid is rectified and fractions of 250—300 grms. collected, at a rate of 4 c.c. per minute, up to  $198^\circ\text{C}$ . The crystallising point of each fraction is then determined, first rapidly on a small quantity in a test-tube and afterwards by slowly cooling 30—40 grms. in a cylinder, supercooling by  $1^\circ$  or  $2^\circ\text{C}$ . and starting crystallisation by adding a little solid phenol; the maximum temperature reached during crystallisation is observed. If in the preliminary determination the crystallising temperature be below  $21^\circ\text{C}$ ., the sample is enriched with a known proportion of phenol crystallising at  $40.2^\circ\text{C}$ ., so as to secure crystallisation at about  $26^\circ\text{C}$ . The proportion of phenol (crystallising at  $40.2^\circ\text{C}$ .) in each fraction is read off on a straight-line freezing-point curve, on which  $40.2^\circ\text{C}$ . is the freezing-point of 100% phenol and  $20^\circ\text{C}$ . that of 66% phenol. The error in a determination is not greater than 1%. —F. SOHN.

*Resorcinol; Colours produced by*—— in solutions of certain salts and their use for the detection of resorcinol in presence of other phenols. F. C. Krauskopf and G. Ritter. J. Amer. Chem. Soc., 1916, 38, 2182—2187.

RESORCINOL produces, in an ammoniacal solution of zinc salts, a blue colour which has been used for the colorimetric estimation of zinc. Colours of a somewhat similar order are, however, produced with cobalt, nickel, and cadmium, so that the reaction is of no value as a qualitative test for zinc. In studying the reaction as a test for resorcinol, it was found that the violet coloration produced with ammoniacal solutions of cobalt is the most intense. If the tubes be tightly stoppered after mixing, the violet colour develops more slowly but remains more stable than when access of air is allowed. This violet coloration is, however, either inhibited or obscured by the presence



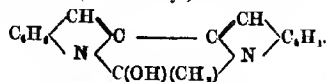
of other phenols and is not adapted for the detection of resorcinol in mixtures. On the other hand, when the test is made under the following conditions, satisfactory indications are obtained with as little as 0.001 grm. of resorcinol.—The solution is mixed in a Nessler tube with 1 c.c. of cobalt chloride solution containing 0.0004 grm. of cobalt, 0.3 c.c. of ammonia solution of sp.gr. 0.90, 3 c.c. of 95% alcohol, and water to 50 c.c. The tube is tightly closed with a rubber stopper, allowed to stand for 3–5 mins. and shaken vigorously. Resorcinol develops a dark green colour, catechol, quinol, and pyrogallol a brown, while phenol remains colourless. The brown colour developed by the other phenols does not interfere with the detection of resorcinol in the presence of substantial quantities of these.—J. F. B.

**Acid chlorides; Photo-chemical decomposition of certain** — S. C. J. Olivier. Rec. Trav. Chim. Pays-Bas, 1916, 36, 117–125.

WHEN *p*-chlorobenzene sulphochloride in ethereal solution is exposed to direct sunlight or the rays of a "Uviol" lamp, chlorine is liberated and oxidation takes place with the formation of the free sulphonic acid. When the experiment is carried out by passing dry oxygen through the ethereal solution of the sulphochloride while exposed to the rays of the lamp, the quantity of chlorine collected shows a deficit as compared with the equivalent of sulphonic acid formed, and aldehyde and hydrochloric acid are found in the aqueous liquid on treatment with water. It is probable, therefore, that some of the chlorine reacts with the ether to form chloroethyl ether, which is subsequently hydrolysed to aldehyde. Under favourable conditions, the decomposition of the sulphochloride under the influence of light and oxygen may amount to over 40% in six hours and the reaction is practically inhibited in the absence of light or oxygen; the presence or absence of moisture has no appreciable influence. The photo-chemical decomposition of the sulphochloride is considerable in ethereal solution but only slight in chloroform solution; in benzene and carbon tetrachloride, the reaction does not take place. It is suggested that the formation of a peroxide may play a part in the reaction. Other sulphochlorides of the benzene series behave in a similar manner in a subordinate degree.—J. F. B.

**Di-indolyl; New derivatives of** — W. Madelung and F. Hager. Ber., 1916, 49, 2039–2050.

By the action of acetic anhydride on di-indolyl under varying conditions, a C-monoacetyl- and an N-mono- and diacetyl-di-indolyl were obtained. N-Diacetyl-di-indolyl is formed in the largest quantity by carrying out the acetylation at ordinary temperatures, and cannot be obtained by the further acetylation of the monoacetyl-derivative. It forms colourless crystals, m.pt. 208° C. The N-monoacetyl-di-indolyl forms the chief product by acetylating at 40°–50° C., and reasons are given for assigning to it the constitution of an N-cycloacetyl-di-indolyl,



To the C-monoacetyl derivative, which was obtained by boiling under a reflux condenser for 4 hours, a similar ring structure is assigned. Unlike the N-compounds, this substance is yellow, and stable towards acids and alkalis. Benzoyl chloride gave with di-indolyl only the dibenzoyl-compound, m.pt. 267° C. It has acid properties, and gives a potassium salt from which enolic ethers were prepared by the action of alkyl iodides. No reduction products of di-indolyl itself could be

isolated, but the reduction of this substance or of C-cyclo-acetyl-di-indolyl with hydrogen iodide in acetic acid solution gave a colourless crystalline basic product,  $\text{C}_{14}\text{H}_{12}\text{N}_2$ , of m.pt. 214° C., to which the name cycloethylidene-tetrahydrodi-indolyl is given.—G. F. M.

**Benzol recovery and rectification.** Walmsley and Morley. See 11A.

**Utilisation of the tar from gas producers using lignite as fuel.** Fischer and Schneider. See 11A.

#### PATENTS.

**Creosote from hardwood-tar oils; Process of producing** — L. F. Hawley, Randolph, N.Y., U.S. Pat. 1,189,271, Sept. 26, 1916. Date of appl. June 8, 1916.

WOOD-TAR oils are treated with sufficient of an alkaline solution to dissolve two-fifths of the phenols present; the resulting solution is distilled, being partly oxidised during the distillation, and the creosote is neutralised and recovered, dissolved in alkali, and again distilled under oxidising conditions.—F. W. A.

**Sulphonic acids; Manufacture of alkali salts of aromatic—**from the corresponding alkaline-earth salts. M. Maxim, Berlin. Ger. Pat. 293,982, Aug. 21, 1915.

THE solution of the alkaline-earth sulphonate is filtered through a layer of granulated alkali aluminosilicate, whereupon an exchange of bases takes place as in the permutite process of water-softening. The residual alkaline-earth aluminosilicate may subsequently be treated with alkali chloride solution to regenerate alkali aluminosilicate.—A. S.

**Bromo- $\alpha$ -hydroxyanthraquinones; Preparation of** — Farb. vorm. Meister, Lucius, u. Brünig. Ger. Pat. 293,694, Dec. 13, 1913.

BROMO-DERIVATIVES of  $\alpha$ -hydroxyanthraquinones, difficult to prepare in other ways, can be obtained by the action of bromine in presence of substances capable of combining with hydrogen bromide. For example,  $\alpha$ -hydroxyanthraquinone yields 1,4-bromohydroxyanthraquinone, m.pt. 197°–198° C.; anthraflavin yields 4,8-dibromo-1,5-dihydroxyanthraquinone, and chrysazin yields tetrabromochrysazin (2,4,5,7-tetrabromo-1,8-dihydroxyanthraquinone).—A. S.

**$\omega$ -Dibromo-*p*-toluyl- $\alpha$ -benzoic acid; Preparation of transformation products of** — [e.g., anthraquinone-2-aldehyde]. Chem. Fabr. Griseheim-Elektron. Ger. Pat. 293,981, July 18, 1914.

ANTHRAQUINONE-2-ALDEHYDE is obtained by heating  $\omega$ -dibromo-*p*-toluyl- $\alpha$ -benzoic acid to a high temperature; or *p*-aldehydobenzophenone- $\alpha'$ -carboxylic acid may be first formed by heating with sulphuric acid at a relatively low temperature and then the temperature raised to convert this into the anthraquinone-aldehyde. Other hydrolysing agents than sulphuric acid, e.g., a dilute alkali solution, may be used to convert the  $\omega$ -dibromo-*p*-toluyl- $\alpha$ -benzoic acid into *p*-aldehydobenzophenone- $\alpha'$ -carboxylic acid, and the latter converted into anthraquinone-2-aldehyde by heating with any suitable dehydrating agent.—A. S.

**Mononitrocarbazoles; Preparation of** — Farb. vorm. Meister, Lucius, u. Brünig. Ger. Pat. 294,010, Sept. 23, 1913.

CARBAZOLE or an N-alkyl, N-aryl, or halogen derivative is dissolved or suspended in an inert medium, immiscible with water, and treated with nitric acid.—A. S.

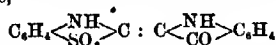
*Furnace using oil or tar as fuel.* Ger. Pat. 293,116. See IIb.

*Manufacture of hard, pale-coloured coumarone resin.* Ger. Pat. 294,107. See XIII.

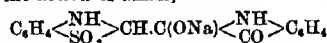
#### \* IV.—COLOURING MATTERS AND DYES.

*Indigo; The chromophor of —.* M. Claass. Ber., 1916, 49, 2079—2095.

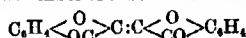
THE possibility or presence of quinonoid linkages is generally accepted for all dyestuffs with the exception of those of the indigoid type, where the chromophor is assumed to be the grouping  $\text{CO}:\text{C}:\text{CO}$ . In accordance with this theory a substance,



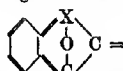
(obtained by condensing isatin chloride with sulphurylindoxyl) might be coloured but would not be a dyestuff, whilst the product derived from it by the action of alkali,



should not even be coloured. Both substances are, however, actually blue dyestuffs. On the other hand a number of substances such as oxindigo



containing the group  $\text{CO}:\text{C}:\text{CO}$  are coloured but are not dyestuffs, whilst there are a number of substances such as Pyrrole Blue, Indophenine Blue, and Isatinpiperidine Blue, which do not contain this group and yet are exceedingly like indigo in all their properties. All indigoid compounds may, however, be regarded as containing at least one inner ring of a betaine-like structure

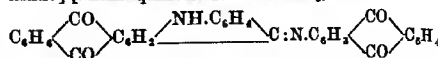


termed indogen, and this constitutes the real chromophor, bringing the indigoid compounds into accordance with the rule that dyestuffs are only produced when the auxochrome so modifies the ring as to produce the maximum of double linkages. Indigo would thus have the constitution represented by two indogen groupings. The inner salt formation may be greatly influenced by the entrance of other groups into the molecule; thus N.N-diacetylindigotin is a reddish compound without any tinctorial properties and hence possesses no internal betaine-like ring, whilst N.N-dimethylindigotin is a dyestuff closely resembling indigo. The fact that indigo cannot be alkylated directly is regarded as confirmative evidence that the nitrogen atoms are present in the form of an internal ammonium salt. Numerous examples from the different classes of indigoid colours are quoted in support of the theory that all truly indigoid dyestuffs, in which class are included such dyestuffs as Pyrrole Blue and Indophenine Blue, contain the indogen chromophor. It is suggested also that many dyestuffs of the anthraquinone series, e.g., Indanthrene, owe their dyeing properties to the presence of a betaine-like chromophor. T. C.

*1-Aminoanthraquinone; Action of o-chlorobenzaldehyde on —.* G. Kalischer and F. Mayer. Ber., 1916, 49, 1994—2000.

*o-[ANTHRAQUINONYL-1-AMINO]-BENZALDEHYDE* is the main product of the action of o-chlorobenzaldehyde on 1-aminoanthraquinone at 200°—

210° C. in nitrobenzene solution. It forms red crystals, m.pt. 254° C. When two mols. of aminoanthraquinone are employed to one of chlorobenzaldehyde, and their solution in nitrobenzene is heated with anhydrous potassium carbonate and a small quantity of copper powder, a bluish-green dyestuff is formed in preponderant amount, to which the constitution of a [1-anthraquinonylimino]-[anthraquinone-2.1-acridone],



is assigned. If the above starting materials are heated with fused potassium acetate and copper powder in naphthalene solution at 225°—230° C. for 8 hours, as described in Ger. Pat. 280,711 (this J., 1915, 545), a blue dyestuff of apparently the same molecular formula as the above, but of undetermined constitution, is produced.—G. F. M.

#### PATENTS.

[Sulphur] dyes and process of making same. H. Heimann, Dessau, Assignor to Act.-Ges. f. Anilinfabr., Berlin. U.S. Pat. 1,199,097, Sept. 26, 1916. Date of appl., Jan. 21, 1915.

SEE Ger. Pat. 293,186 of 1914; this J., 1916, 1050. The dyestuff obtained by the action of sulphur on p-nitrobenzeneazo-N-ethyl-a-naphthylamine is specially claimed. It is easily soluble in alkali sulphide and alkaline hydrosulphite solutions, and gives on unmordanted cotton yellowish-brown tints fast to washing and to boiling dilute acids.

*o-Hydroxydisazo dyestuffs; Manufacture of chrome —.* Act.-Ges. f. Anilinfabr. Ger. Pat. 293,657, July 29, 1915.

NITRO-2-AMINOPHENOLS or their sulphonic acids are diazotised and combined with 2-amino-5-naphthol-7-sulphonic acid in alkaline solution, and the intermediate products are again diazotised and then combined with alkylaralkylarylaminesulphonic acids. The products dye wool, the shades produced after chroming being black and of excellent fastness to light, washing, and milling.—A. S.

*Trisazo dyestuffs; Manufacture of —.* Act.-Ges. f. Anilinfabr. Ger. Pat. 293,659, June 5, 1915.

A 4,4'-DIAMINOAZO compound is diazotised and combined with 1 mol. of a 1,8-dihydroxynaphthalenesulphonic acid and 1 mol. of a m-diamine, or a 4'-nitro- or 4'-acidylamino-1-aminoazo compound is diazotised, coupled with a 1,8-dihydroxynaphthalenesulphonic acid, and then, after reducing the nitro group or eliminating the acidyl group, the product is again diazotised and coupled with a m-diamine. Black to bluish-black shades are obtained from the resulting trisazo dyestuffs by after-treatment on the fibre.—A. S.

*Trisazo dyestuffs; Manufacture of diazotisable —.* Act.-Ges. f. Anilinfabr. Ger. Pat. 293,858, June 30, 1915.

A DIAZOSULPHONIC acid of the benzene or naphthalene series is combined with a suitable middle component, the product is diazotised and combined with a-naphthylamine or 1-aminonaphthalene-6- or -7-sulphonic acid, and the resulting disazo compound is diazotised and combined with 2-amino-8-naphthol-6-sulphonic acid in alkaline solution. The products are useful for producing level grey shades on cotton. When diazotised on the fibre and combined with compounds such as g-naphthol or m-toluylenediamine, grey shades fast to washing, light, and alkalis are obtained. The shades are faster to light than those produced by Diaminogen B.—A. S.

[Azo] wool dye. P. Hauptmann, Leverkusen, Germany. Assignor to Synthetic Patents Co., New York. U.S. Pat. 1,199,890, Oct. 3, 1916. Date of appl., Jan. 20, 1915. Renewed Aug. 19, 1916.

Azo dyestuffs dyeing wool in acid baths yellow to bluish-red to brown shades, fast to fulling, are obtained by coupling azo dyestuff components with the diazo derivative of an arylenediamine of the benzene series, one of the amino groups of which is disubstituted by an acyl group and an organic radicle respectively. The dyestuffs from substituted toluylenedianines and naphtholsulphonic acids are dark powders, soluble in water, which give, generally, reddish shades on wool.—A. S.

Trisazo dyestuffs; *Manufacture of*—, Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 293,658, July 11, 1914. Addition to Ger. Pat. 293,184.

THE process described in the chief patent (this J., 1916, 922) is modified by using 2-amino-5-naphthol-7-sulphonic acid as end component instead of 2-amino-8-naphthol-6-sulphonic acid, and by effecting the final coupling in slightly acid solution. The products are faster to light than Neutral Grey.—A. S.

Nitrosamines of primary aromatic amines and their alkali salts; *Manufacture of*—, Chem. Fabr. Griesheim-Elektron. Ger. Pat. 292,118, Aug. 29, 1915.

NITROSAMINES of primary aromatic amines are obtained in the form of their alkali salts by the action of caustic alkalis on the arylsulphonates of the corresponding diazo or tetrazo compounds in separated, concentrated form.—A. S.

Dianthraquinonylene diorides; *Manufacture of*—, Farb. vorm. Meister, Lucius, u. Brünig. Ger. Pat. 293,660, May 6, 1914.

6-NITROHYDROXYANTHRAQUINONES are heated with alkaline condensing agents at a high temperature. The products, which are formed by the union of two mols. of the anthraquinone derivative with elimination of two mols. of nitrous acid, are either vat dyestuffs or may be used in the manufacture of dyestuffs.—A. S.

Vat dyestuffs of the anthraquinone [Indanthrene] series; *Manufacture of blue—containing chlorine and fast to chlorine*. Farb. vorm. Meister, Lucius, u. Brünig. Ger. Pat. 293,971, June 3, 1914. Addition to Ger. Pat. 287,590 (this J., 1916, 171).

N-DIHYDRO-1,2,2',1'-ANTHRAQUINONEAZINE (Indanthrene) is heated under pressure, at a temperature not exceeding about 170°C., with sulphuryl chloride, with or without addition of indifferent diluents.—A. S.

Vat dyestuffs of the anthraquinone series; *Manufacture of*—, R. Wedekind und Co., Uerdingen. Ger. Pat. 293,970, Dec. 28, 1913.

1-CHLORO-2-HYDROXYANTHRAQUINONE, a salt of anthraquinone-2-sulphonic acid, or the yellow vat dyestuff prepared from 1-chloro-2-hydroxyanthraquinone as described in Ger. Pat. 257,832 (this J., 1913, 481) is heated with dry alkali sulphide above 220°C., and the products, which are insoluble in water, alkalis, and alkali sulphides, are chlorinated.—A. S.

Sulphurylindoxyl; *Preparation of*—, M. Claass, Banzig-Langfuhr. Ger. Pat. 294,084, Jan. 27, 1916.

SULPHURYLINDOXYL is obtained by heating sulphazone with ammonia at a high temperature, under pressure. It combines with isatin or its derivatives to form valuable vat dyestuffs. (See also this J., 1916, 529, 1104.)—A. S.

o-[Hydroxy]disazo dyestuffs; *Manufacture of chromable secondary*—, M. Boeniger, Assignor to Chemical Works formerly Sandoz, Basle, Switzerland. U.S. Pat. 1,199,233, Sept. 26, 1916. Date of appl., Jan. 29, 1916.

SEE Eng. Pat. 17,607 of 1915; this J., 1916, 531.

Disazo dyestuffs; *Manufacture of chromable secondary*—, M. Boeniger, Assignor to Chemical Works formerly Sandoz, Basle, Switzerland. U.S. Pat. 1,199,234, Sept. 26, 1916. Date of appl., May 13, 1916.

SEE Eng. Pat. 100,472 of 1916; this J., 1916, 733.

Gallocyanine dyestuffs; *Halogen derivatives of— and process of making same*. G. Engi, Assignor to Soc. of Chem. Ind. in Basle, Switzerland. U.S. Pat. 1,199,458, Sept. 26, 1916. Date of appl., Nov. 10, 1915.

SEE Eng. Pat. 14,159 of 1915; this J., 1916, 628.

Nitrosamines of primary aromatic amines; *Process for the manufacture of alkali salts of*—, M. Hankel, Offenbach, Assignor to Chem. Fabr. Griesheim-Elektron, Frankfurt, Germany. U.S. Pat. 1,200,726, Oct. 10, 1916. Date of appl., Dec. 3, 1915.

SEE Ger. Pat. 292,118 of 1915; preceding.

Vat dye [of the naphthalene series] and process of making it. M. Kardos, Charlottenburg, and P. Nawiasky, Assignors to Badische Anilin und Soda Fabr., Ludwigshafen, Germany. U.S. Pat. 1,200,848, Oct. 10, 1916. Date of appl., Sep. 10, 1914.

SEE Ger. Pat. 276,956 of 1913; this J., 1914, 1084.

## V.—FIBRES; TEXTILES; CELLULOSE; PAPER.

Wood; *The colour-producing constituents of*—, H. Wichelhaus and M. Lange, Ber., 1916, 49, 2001.

THE hydrolytic decomposition of wood by means of superheated steam at 180°C. gave a distillate from which, by extraction with ether, an oil was obtained which gave with phloroglucinol and hydrochloric acid a colouring matter apparently identical with that produced on wood itself with these reagents. The aqueous liquid after extraction with ether gave under similar treatment a pale red coloration which eventually became greenish-brown.—G. F. M.

Wood pulp; *The resin of coniferous woods and the de-resinification of*—, R. Sieber. Schriften des Vereins der Zellstoff- u. Papierchem., Bd. 9, Z. angew. Chem., 1916, 29, Ref., 429—430.

THE so-called resin isolated from pine wood by extraction with organic solvents, contains, on the average, 50% of fatty matter. Only traces of turpentine can be extracted from freshly-cut, relatively young wood by extraction with ether, but when the same wood is boiled with caustic soda solution under a pressure of 8 atmospheres, the vapours discharged during the "blowing-off" operation contain measurable quantities of turpentine. The "resin" extracted from sulphite-pulp by ether and alcohol contains respectively 63 and 74% of fatty matter, and it is to this fatty matter that the so-called "resin specks" (this J., 1908, 438) on paper made from sulphite pulp are due.—A. S.

Liquid Swedish resin [from wood pulp waste lyes]. Lorentz. See XLIII.

Brewers' filter pulp. Foster. See XVIII.

*Abnormal adsorption [of hydrochloric acid] by filler paper.* Murray. See XXIII.

#### PATENTS.

*Ungumming silk and silk wastes; Bath for —.* P. Schmid and K. Gross, Basle, Switzerland. U.S. Pat. 1,199,433, Sept. 26, 1916. Date of appl., Oct. 7, 1915.

SEE Eng. Pat. 100,029 of 1916; this J., 1916, 733. An aqueous solution containing  $\frac{1}{2}$  to 6 parts of soap and  $9\frac{1}{2}$  to 4 parts of silkworm chrysalides is specified.

*Cellulose esters insoluble in chloroform and their products of transformation; Process for the manufacture of —.* H. Dreyfus. Fr. Pat. 478,023, Nov. 11, 1914. Under Int. Conv., Oct. 12, 1914.

IN order to produce chloroform-insoluble cellulose acetate of maximum viscosity, the acetylating mixture should be cooled sufficiently during the early stages of the reaction to keep it preferably below 5° C. Later on it may be allowed to rise slowly to 30°–35° C. and should then be cooled again to 25°–30° C. These limits of temperature are more easily observed if the amount of acetic anhydride or other acetylating agent is less than three times the weight of the cellulose. The weight of sulphuric acid should be from 5% to 20% of the weight of cellulose. Similar precautions as to temperature should be observed in acetylating cellulose suspended in toluol or benzol, or when the sulphuric acid is replaced by other condensing agents in sufficient quantity to produce the same effect. *Example:* A mixture of 300–400 kilos. of glacial acetic acid, 250 kilos. of acetic anhydride, and 10–15 kilos. of concentrated sulphuric acid is cooled to below 0° C., e.g., to –3° C., which causes the acetic acid to crystallise; 100 kilos. of cotton or paper of normal humidity (3–6%) is introduced and the mixture well stirred. The temperature rises after some time to 5°–15° C., and then falls to 5°–10° C. The cooling may then be stopped, and the temperature allowed to rise to 15°–20° C., or even to 25°–35° C., but if allowed to rise higher the viscosity of the product will be diminished. Cooling is then recommenced, with constant stirring, until the temperature of the mass begins to fall, and the mixture is then allowed to stand until all the fibres, and any crystalline substances formed during the cooling, have disappeared. The product may be separated by any of the known methods, or the reaction may be allowed to proceed further, with addition of water, etc., to modify the solubility of the product. (Compare Fr. Pat. 432,046 and Additions thereto; this J., 1912, 24, 329; 1913, 283, 420.)—F. Sp.

*Artificial silk; Process and apparatus for spinning — in the air.* Soc. La Setaoid. Fr. Pat. 478,315, July 25, 1914.

FOR spinning twisted artificial silk from nitrocellulose solutions of which the threads solidify almost immediately in the air (see following abstract), a central cylindrical solution reservoir of adjustable height is provided with several taps fitted with spinnerets. Each spinneret contains a number of tubes, converging towards their lower ends, and terminating in capillary orifices. Vertically below each spinneret is a small rotating table, with a central rod projecting vertically from it. The threads of nitrocellulose issuing from the converging orifices of the spinneret stick together and descend on to the rotating table, the effect of which is to twist the threads on each other, and to wind them round the rod on the table in the form of a vertical cocoon, in a convenient shape for denitration, etc. The vertical distance between

the reservoir and the rotating tables is adjusted to suit the solution and the atmospheric conditions.—F. Sp.

*Threads having the appearance of silk; Process for obtaining —.* Soc. La Setaoid. Fr. Pat. 478,461, July 27, 1914.

A SUITABLE solution for use in the spinning apparatus described in the preceding abstract is obtained by adding to 10 kilos. of nitrocellulose solution, 300 grms. of anhydrous aluminium chloride, 100 grms. of purified aluminium chloride, 80 grms. of sodium formate, 200 grms. of aluminium phosphate, and 80 grms. of aluminium nitrate. Water, alcohol, or ether may be added according to the fluidity desired. The product is adapted for spinning in the air, and yields threads resembling silk in appearance and possessing considerable resistance to humidity.—F. Sp.

*Cork; Preparation of moulded objects of —.* Rheinhold und Co., Vereinigte Norddeutsche und Dessauer Kieselguhr-Ges., Hanover. Ger. Pat. 294,072, Oct. 30, 1913.

THE particles of cork are mixed with a suitable binding agent, moulded into shape, then coated with a suitable fireproof material, e.g., water-glass, aluminium sulphate, lime, or the like, and heated above 200° C. Alternatively, the cork particles may be mixed with clay or other fire-resisting material and water or other suitable liquid, moulded, dried, and heated above 200° C.—A. S.

*Decortication and scouring of urticaceous plants; Process for the —.* O. Richter and F. Pick, Vienna. U.S. Pat. 1,201,101, Oct. 10, 1916. Date of appl., Feb. 2, 1915.

SEE Ger. Pat. 284,704 of 1914; this J., 1915, 1048.

*Cellulose acetates and conversion products; Manufacture of —.* H. Dreyfus, Basle, Switzerland. Eng. Pats. (A) 14,101, Oct. 5, 1915, and (B) 101,555, Oct. 5, 1915 (Appl. No. 13,447 of 1916). Under Int. Conv., Oct. 12, 1914.

SEE Fr. Pat. 478,023 of 1914; preceding. (B) Reference is directed, in pursuance of Sect. 7, Sub-sect. 4, of the Patents and Designs Act, 1907, to Eng. Pat. 20,977 of 1911.

*Cellulose derivatives [viscose]; Treatment of —.* F. Steimmig, Hanover, Germany. U.S. Pat. 1,200,774, Oct. 10, 1916. Date of appl., June 12, 1913.

SEE Fr. Pat. 458,979 of 1913; this J., 1913, 1153.

*Celluloid; Composition of matter resembling —.* O. Schmidt, Assignor to Badische Anilin und Soda Fabr., Ludwigshafen, Germany. U.S. Pat. 1,200,886, Oct. 10, 1916. Date of appl., Oct. 21, 1914.

SEE Eng. Pat. 9270 of 1914; this J., 1915, 867. A mixture containing nitrocellulose and acetylhydrotoloxylamine is specially claimed.

*Condensation products [from phenols and formaldehyde] and method of manufacturing a substance capable of replacing ivory, mother of pearl, celluloid, etc.* Fr. Pat. 478,884. See XIII.

*Varnishes with a basis of cellulose acetate.* Fr. Pat. 479,387. See XIII.

#### VI.—BLEACHING; DYEING; PRINTING; FINISHING.

*Nitre cake in the textile industries.* P. Beaumont, Manchester Chem. Club, Oct. 27, 1916. Chem. Trade J., Nov. 4, 1916.

THE supply of sulphuric acid to bleachers, dyers, and calico printers was cut off some months ago,

and in September these consumers were informed by the Ministry of Munitions that on and after Oct. 18th all supplies of hydrochloric acid would be stopped, and that nitre cake must be used in its place; this time limit was afterwards extended to October 30th. In spite of statements to the contrary, in many cases it is not possible to bleach successfully without using hydrochloric acid: this applies particularly to goods in which the highest degree of whiteness and purity was demanded. Certain classes of goods, including those which have to be dyed or printed with alizarin colours, can only be bleached successfully if they are subjected to the lime boil, in which case it is essential to use hydrochloric acid for souring. In many cases a caustic soda boil could replace the lime boil, but then the increased demand for soda would render the position even more difficult. The use of nitre cake in textile operations involves a great deal of extra work and extra space, especially in connection with freeing the solution from dirt. If nitre cake has to be used it will involve either a considerable reduction in the bleaching of cotton and linen, or trouble between bleachers and dyers owing to damage.

In the discussion it was stated that the Government was prepared to supply hydrochloric acid in cases in which it was not possible to use nitre cake. Two of the speakers stated that nitre cake had been used by their firms with success.

*Staining of tissue with the simplest dyestuffs, and their fixation.* S. Skraup. Ber., 1916, 49, 2142—2154.

ALL basic dyestuffs used as stains may be fixed by the use of mercuric chloride, due to the production of mercuramino compounds, and generally every dyestuff used for staining tissue may be fixed by selecting a fixing agent which converts it into an insoluble compound. Dyestuffs containing hydroxyl groups may, for example, be fixed with lead acetate. No specific chemical constitution can be found which gives a substance the property of staining tissue, as this property is possessed by even the simplest dyestuffs. The colloidal condition shown by previous researches to be necessary for staining is markedly affected by even slight variations in chemical constitution.—F. W. A.

#### PATENTS.

*Dyeing; Process of* —. I. J. Smith, McNamara, and H. B. Smith, Albany, N.Y., Assignors to Surpass Chemical Co. U.S. Pat. 1,199,745, Sept. 26, 1916. Date of appl., Mar. 21, 1916.

UNCOMBED cotton material is treated with an alkaline oxidising bath to soften any notes, shives, and/or leaf present, the bath also containing a direct or vegetable dyestuff unaffected by the other substances present.—F. W. A.

*Dyeing apparatus.* D. M. Hey, Assignor to Vacuum Dyeing Machine Co., Chattanooga, Tenn. U.S. Pat. 1,199,982, Oct. 3, 1916. Date of appl., Apr. 5, 1910.

THE material to be dyed is placed in the dye vat between two perforated plates. Dye liquor is discharged into the space beneath the lower perforated plate from a distributor with radial arms, and after passing through the material overflows from the space above the upper perforated plate into a relatively shallow conduit which extends round the chamber, and communicates with the suction side of the circulating pump.—F. W. A.

*Fabric-treating apparatus.* T. Allsop and W. W. Sibson, Assignors to The Philadelphia Drying Machinery Co., Philadelphia, Pa. U.S. Pat. 1,200,433, Oct. 3, 1916. Date of appl., Oct. 5, 1914.

A FABRIC-TREATING apparatus consists of a tank

through which extends a perforated pipe for delivering or withdrawing liquor; a perforated drum divided into pockets by perforated radial walls is mounted on this pipe as axis and may be rotated submerged in the liquor in the tank; a second perforated pipe, provided at the end with a removable cap, extends along the bottom of the tank, outside the drum, and means are provided for circulating the liquor in either direction; the tank has an opening in one of its walls closed by a panel.—F. W. A.

*Dyeing apparatus.* W. A. Traver, Assignor to Franklin Process Co., Providence, R.I. U.S. Pat. 1,200,546, Oct. 10, 1916. Date of appl., Feb. 18, 1916.

A HOLLOW tubular perforated stringer, suitable for holding a number of dye-cops strung along its length, has a non-perforated section at one end, and this section is formed with peripheral grooves spaced apart. A flange is adapted to slide on the stringer and compress the yarn in the cops, and is held in place by a plate adjustable laterally across the flange to engage the grooves in the end of the stringer.—F. W. A.

*Dyeing machine.* F. S. Williams, Assignor to Klauder-Weldon Dyeing Machine Co., Amsterdam, N.Y. U.S. Pats. 1,200,677 and 1,200,678, Oct. 10, 1916. Date of appl., Feb. 10, 1915.

DEVICES for rotating the yarn sticks are claimed.

*Dyeing apparatus.* L. P. Hart. Fr. Pat. 478,234, Apr. 1, 1915.

IN order to ensure thorough mixing of the dye-liquor, it is introduced inside hollow non-perforated rollers, open at the ends, carrying the material to be dyed.—F. W. A.

*Cotton dyed with sulphur dyestuffs; Process for preventing tendering of — in union goods.* Act.-Ges. f. Anilinfabr. Ger. Pat. 293,455, June 30, 1914.

THE material, after dyeing with a sulphur colour, is treated with ammonium salts and chromates, whereby the wool is dyed and the cotton is prevented from tendering.—A. S.

*Calcium soaps in washing baths; Process for preventing flocculation of —.* Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 294,028, Oct. 15, 1914.

A COLLOID soluble in water is added to the bath with the soap. Suitable substances are glue, albumin or its cleavage products, vegetable glue from carrageen moss, and sulphite-cellulose waste lyes in which the lime has been replaced by alkali.—A. S.

*Dyeing with dyestuffs insoluble in water or water-insoluble leuco-compounds of dyestuffs; Process for —.* M. Iljinsky, Assignor to Wedekind and Co., Uerdingen, Germany. U.S. Pat. 1,199,273, Sept. 26, 1916. Date of appl., Dec. 10, 1912.

SEE Fr. Pat. 451,533 of 1912; this J., 1913, 598.

*Sericin soap for dyeing silk, silk-spuns, and silk tissues; Process for the manufacture of a substitute for —.* P. Schmid and K. Gross, Basle, Switzerland. U.S. Pat. 1,199,131, Sept. 26, 1916. Date of appl., Oct. 7, 1915.

SEE Eng. Pat. 101,169 of 1916; this J., 1916, 734.

*Sulphur dyes; Process of making [pastes for dyeing with —].* E. Voetter, Bockum, Germany. U.S. Pat. 1,200,055, Oct. 3, 1916. Date of appl., Feb. 26, 1907.

SEE Eng. Pat. 8966 of 1906; this J., 1907, 16.

*Reserve style of printing or dyeing chrome-dyestuffs.*

Durand und Huguenin A.-G., Basle, Switzerland. Eng. Pat. 100,885, June 14, 1916 (Appl. No. 8409 of 1916). Under Int. Conv., July 12, 1915.

SEE Ger. Pat. 293,359 of 1915; this J., 1916, 1058.

## VII.—ACIDS; ALKALIS; SALTS; NON-METALLIC ELEMENTS.

*Phosphoric acid evolved in the volatilisation method of treating phosphate rock; Use of the Cottrell precipitator in recovering —* W. H. Ross, J. N. Carothers, and A. R. Merz. U.S. Bureau of Chem. Oil, Paint, and Drug, Rep., Oct. 2, 1916.

THE authors have applied the Cottrell method of electrical precipitation (this J., 1911, 1037) to the recovery of the phosphorus pentoxide volatilised on heating a mixture of phosphate rock, coke, and sand. The charge is heated in an electric furnace, and the volatilised phosphorus pentoxide is carried by a current of air to the precipitation apparatus, which it enters at a temperature above 100° C. It is stated that phosphoric acid of 99.89% purity is thus obtained in the form of a highly concentrated solution (np to 92%).

### Potash deposits in Cuba.

AMERICAN newspapers recently contained reports to the effect that extensive deposits of potash salts had been discovered near Motembo, Cuba, and a company was formed, with a capital of \$5,000,000, to work the deposits, which were stated to contain up to 40% K<sub>2</sub>O. The Cuban Government Engineer has examined the property and has analysed thirteen samples from the alleged deposits, but the highest result he obtained was only 0.51% of potash.

*Nitrogen works in Sweden.* Engineering, Nov. 3, 1916.

A COMPANY with a large capital has been formed in Sweden to manufacture nitric acid and other products by the Birkeland-Eyde process. Works are to be erected at Trollhättan, where the power station will supply 12,000 k.w. of energy. The annual capacity of the plant will be about 7000 tons of concentrated nitric acid. The works are guaranteed to be ready this year.

*Chlorides [; Volumetric determination of —] in presence of thiocyanates.* F. W. Bruckmiller. J. Amer. Chem. Soc., 1916, 38, 1953—1955.

IN solutions containing both chlorides and thiocyanates, the former may be determined volumetrically with silver nitrate, using chromate indicator, after decomposing the thiocyanate by boiling with a small quantity of nitric acid for 15 mins. The solution is cooled, and neutralised with sodium bicarbonate, using methyl orange as indicator, before titrating with silver nitrate. No loss of hydrochloric acid occurs under these conditions, and the hydrocyanic acid formed by decomposition of the thiocyanate is expelled to within 3 mgrms. per litre, an amount which is practically negligible. Moreover no sulphur compounds are formed which can interfere with the silver nitrate titration. It was incidentally determined that the chromate indicator can be used in acid solutions provided the hydrogen ion concentration is not greater than 0.0028 N.—G. F. M.

*Hydrogen sulphide; Action of — on mixtures of the alkaline earths with the alkalis and with oxides of the heavy metals.* II. I. Guareschi. Atti R. Acad. Sci. Torino, 1915—1916, 51, 951—962. J. Chem. Soc., 1916, 110, ii., 529. (Compare this J., 1916, 835, 836.)

THE effect of strontium and lithium oxides on the

action of hydrogen sulphide on sodium hydroxide or potassium hydroxide is considerably less energetic than that of calcium oxide or barium oxide, no incandescence being observed under the conditions used. The incandescence obtained with mixtures of sodium (or potassium) hydroxide and calcium (or barium) oxide cannot be attributed to the presence or formation of peroxides. The alkali peroxides (not, however, of recent preparation) act almost like the hydroxides, whilst barium, magnesium, and lead peroxides have no action. Mixtures of calcium (or barium) oxide with mercuric or nickel oxide also react vigorously with hydrogen sulphide and, when the constituent oxides are in definite proportions, vivid incandescence or even explosion takes place. When incandescence occurs with mercuric oxide, sulphur dioxide is formed, and this reacts with the hydrogen sulphide, giving colloidal sulphur. No incandescence is observed when hydrogen sulphide acts on pumice and mercuric oxide, or on a mixture of calcium (or barium) oxide with ferric oxide, cuprous or cupric oxide, or MnO<sub>2</sub>.

*Mercuric iodide; Action of hydrogen sulphide on —* G. Franceschi. Boll. Chim. Farm., 1916, 55, 481—483. J. Chem. Soc., 1916, 110, ii., 530.

STUDY of this reaction in alcoholic solution shows that it takes place in three phases, with formation of three different compounds, according to the conditions. These phases may be represented thus: (1)  $H_2S + 2HgI_2 = 2HgI + 2HI + S$ ; (2)  $6HgI + H_2S + 4S = 2(2HgS, HgI_2) + 2HI$ ; and (3)  $2HgS, HgI_2 + H_2S = 3HgS + 2HI$ . The action of hydrogen sulphide on mercuric and mercurous salts always yields mercuric sulphide, the mercurous salts being previously reduced to mercurous salts, and an intermediate compound formed which may be regarded as a thiobasic mercury compound of the constitution  $Hg(S, HgR)_2$ . The compound  $Hg(S, HgI)_2$  forms a brown precipitate.

*Copper sulphates; Basic —* S. W. Young and A. E. Stearn. J. Amer. Chem. Soc., 1916, 38, 1947—1953.

BASIC copper sulphates were prepared by allowing finely powdered copper oxide to act on solutions of copper sulphate until equilibrium was attained. This required about 3 months at 25° C. and two weeks at 50° C. The composition of the products was independent of the temperature and the evidence indicated that they were not definite compounds, but rather formed a three-component system in which the components, CuO, SO<sub>3</sub>, and H<sub>2</sub>O varied continuously within certain limits, the most basic salt being probably the compound  $CuSO_4 \cdot 2CuO \cdot 2H_2O$ . In the products of lower basicity the water content increases as the CuO decreases, but it is not certain whether this holds good throughout the whole range to  $CuSO_4 \cdot 5H_2O$ . Basic sulphates, prepared by heating copper sulphate with varying relative amounts of water, are not definite compounds as has been maintained. The formation of a metastable series of basic sulphates, under at present undetermined conditions, was indicated. It is obvious from the above facts that the mineral brochantite will show a variable composition according to the conditions of its formation.—G. F. M.

*Lead arsenates.* I. C. C. McDonnell and C. M. Smith. J. Amer. Chem. Soc., 1916, 38, 2027—2038.

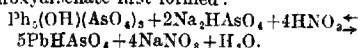
MONOPLUMBIC orthoarsenate,  $PbH_4(AsO_4)_2$ , was prepared by boiling diplumbic arsenate with aqueous arsenic acid of at least 86% strength. It forms long rhomboidal plates, and is completely resolved by contact with water into diplumbic arsenate and arsenic acid. It loses half its water of constitution when heated at 150° C., with the

probable formation of  $\text{PbH}_2\text{As}_2\text{O}_7$ . At a temperature somewhat below that of red heat it is resolved into lead meta-arsenate,  $\text{Pb}(\text{AsO}_3)_2$ , which was also prepared in crystalline form by fusing arsenic acid with litharge. This compound is also decomposed by contact with water. Diplumbic orthoarsenate was prepared by precipitation from lead nitrate or lead acetate solutions with potassium dihydrogen arsenate, and was obtained as long slender crystals from a saturated solution in nitric acid by gradual neutralisation with ammonia vapour from concentrated ammonia solution placed under a bell jar. A crystalline product was also obtained by pouring a boiling saturated solution in nitric acid into six times its volume of boiling water. At  $280^\circ\text{C}$ . it is converted into diplumbic pyroarsenate,  $\text{Pb}_2\text{As}_2\text{O}_7$ . Triplumbic orthoarsenate,  $\text{Pb}_3(\text{AsO}_4)_2$ , has a very limited range of existence. It was not obtained by any precipitation reaction, but a yellowish-brown crystalline mass was produced by fusing diplumbic arsenate with litharge in theoretical proportions.

—G. F. M.

**Lead arsenates.** Study of the factors controlling the reactions of lead nitrate and lead acetate with disodium arsenate. G. E. Smith. J. Amer. Chem. Soc., 1916, 38, 2014—2027.

LEAD arsenates produced by the reaction of lead nitrate or acetate with disodium arsenate are mixtures of diplumbic arsenate,  $\text{PbHAsO}_4$ , and lead hydroxyarsenate,  $\text{Pb}_2(\text{OH})(\text{AsO}_4)_2$ . At low temperatures, when equilibrium has been attained, the product is mainly diplumbic arsenate which is produced by a secondary reaction from the hydroxyarsenate first formed:



An analogous reaction occurs when lead acetate is employed instead of the nitrate. The lead hydroxyarsenate can actually be isolated by carrying out the reaction at great dilution (less than 0.001 mol.) and filtering off the precipitate immediately after its formation. As the concentrations increase, the above equilibrium is displaced towards the right and the composition of the precipitate on attainment of equilibrium more nearly approaches that of diplumbic arsenate; increase in temperature causes the reverse effect. Contrary to expectation an excess of the alkaline disodium arsenate increases the amount of lead hydroxyarsenate produced, its normal effect being apparently masked by the effect of its alkalinity.

—G. F. M.

**Colloidal arsenates and phosphates of iron.** H. N. Holmes and R. E. Rindfusz. J. Amer. Chem. Soc., 1916, 38, 1970—1982.

PRECIPITATED ferric arsenate and phosphate, washed free from adsorbed ions after mechanical disintegration with sand, are soluble in comparatively small amounts of ammonia or the hydroxides of certain other bases, with the formation of deep red sols which on long continued dialysis give excellent gels, the composition of which corresponded closely with the formula  $\text{Fe}(\text{AsO}_4)_3 \cdot \text{Fe}_2\text{O}_3 \cdot 2\text{H}_2\text{O}$ . The colloid formed by using methylamine gives a gel of a deeper red colour than the others. Ferric orthoarsenate or orthophosphate is also peptised by ferric chloride solution, and yields a red gel on dialysis after removal of most of the chloride ion, and similar gels are formed from ferric chloride and the precipitated phosphates or arsenates of any of the common metals. In both these cases of peptisation by salts the action is due to acid hydrolysis, the free acid giving equally good results, but the gel is lighter in colour. If the sulphate is used instead of the chloride a stable sol is formed which

settles out, however, on dialysis. Ferric meta- and pyro-phosphates and ferric arsenite are similarly peptised by ammonia and by ferric chloride. The formation of the sol and gel in acid peptisations is due to the disturbance of the equilibrium by dialysis, since good gels may also be formed by dialysing dilute mixtures of ferric chloride solution and arsenic or phosphoric acids.—G. F. M.

**Hydrogen peroxide; Catalytic decomposition of — in certain non-aqueous solutions.** J. H. Walton and De W. O. Jones. J. Amer. Chem. Soc., 1916, 38, 1956—1961.

COMPOUNDS such as metallic acetates and iodides, cupric, ferric, and manganous chlorides, etc., which catalytically decompose aqueous solutions of hydrogen peroxide, also behave in a similar way towards solutions of the peroxide in amyl alcohol, amyl acetate, isobutyl alcohol, and quinoline. For example a solution of "perhydrol" in quinoline is decomposed quantitatively by manganous acetate. If the catalyst is present in so small a concentration that the reaction requires some hours, only about 75% of the oxygen is evolved, the remainder being utilised in oxidising the quinoline, a reaction which is also appreciably catalysed by the manganous acetate. If the quinoline is saturated with water the catalytic decomposition of hydrogen peroxide is a reaction of the first order, as in aqueous solution, but when only about 2% of water is present, the velocity constant is that of a bimolecular reaction. In solutions containing high concentrations of catalyst, the reaction velocity is approximately doubled by doubling the concentration of the catalyst.—G. F. M.

**Ozonisation of liquid oxygen by radiation.** E. Warburg. Ber. Deut. physik. Ges., 1915, 17, 194—197. J. Chem. Soc., 1916, 110, ii., 526—527.

SMALL quantities of ozone are formed by the action of ultra-violet radiation on oxygen at atmospheric pressure, but since rays of wave-length exceeding  $0.2\mu$  are only slightly absorbed by oxygen under these conditions, it was considered possible that larger quantities might be obtained by the use of liquid oxygen. Experiments made with liquid oxygen and air exposed to the rays emitted by the spark discharge between zinc electrodes, show that appreciable quantities of ozone are formed after a short exposure.

**The Messerschmitt process for the production of hydrogen.** H. L. Barnitz. Met. and Chem. Eng., 1916, 15, 494—498. See page 1137.

**New method for purification of colloidal solutions.** Wegelin. See I.

**Nitre cake in the textile industries.** Bean. See VI.

**Nature of the phosphates contained in mineral phosphates.** Robertson. See XVI.

**Efficiency of calcium chloride, sodium hydroxide, and potassium hydroxide as drying agents.** Baxter and Starkweather. See XXIII.

**Loss of phosphoric acid during fusion with ammonium fluoride.** Davis and Prescott. See XXIII.

**Influence of strong salt solutions on the spontaneous oxidation of pyrogallol, ferrous sulphate, and lactulose.** MacArthur. See XXIV.

#### PATENTS.

**Sulphuric acid; Continuous concentration of —.** S. Dreyfus. Eng. Pat. 101,612, Jan. 7, 1916. (Appl. No. 289 of 1916.)

SULPHURIC acid of about 92% strength is further



concentrated by evaporation in externally heated cast-iron vessels, on which acid of this strength has no action. These vessels each consist of an outer cylindrical cast-iron pan fitted with a lid and containing a series of concentric cylinders alternately supported by the pan and the lid. The acid to be concentrated is fed into the innermost space and passes alternately downwards and upwards to the outermost space, which it leaves by an overflow pipe.—B. V. S.

*Oxalic acid; Process of producing — from sugar and other carbohydrates.* E. R. von Porthelm, Prague, Austria. Eng. Pat. 101,680, Oct. 7, 1915. (Appl. No. 7863 of 1916.)

THE preliminary treatment of the sugar with nitrous gases, to avoid the danger of overheating, as described in Eng. Pat. 14,234 of 1915 (this J., 1916, 889), is extended to other methods of producing oxalic acid from carbohydrates by oxidation. The temperature attained in the preliminary treatment is easily regulated by adjusting the rate of flow of the nitrogen oxides, and very little heat is evolved in the subsequent oxidation to oxalic acid.—B. V. S.

*Caustic polish; Electrolytic manufacture of —.* C. P. Rolland. Fr. Pat. 478,371, July 28, 1914.

A SOLUTION of potassium sulphate is electrolysed using a soluble anode, both electrodes being preferably of iron, thus obtaining potassium hydroxide and hydrogen at the cathode, and a mixture of potassium and iron sulphates, which may be utilised as manure, at the anode. The latter is preferably formed of waste iron clippings, and the cathode of iron sheets placed near to each other and covered by a bell.—B. N.

*Cuprous oxide; Process for the production of — electrolytically.* B. Hunt, Glasgow. Eng. Pat. 14,310, Oct. 9, 1915.

IN the production of cuprous oxide by the electrolysis of a sodium chloride solution between copper electrodes, the colour and uniformity of the product is improved by the addition of sodium nitrate and by heating the solution. A solution containing 10% of sodium chloride and 5% of sodium nitrate, maintained at a temperature of 100° C., is found to work well. The nitrate concentration is kept up by continuous addition of fresh salt; it is reduced to sodium nitrite, which is separated at intervals by cooling and crystallising.—B. V. S.

*Aluminium nitride; Preparation of — in electric arc furnaces.* Aluminium Industrie A.-G. First Addition, dated Feb. 3, 1915 (under Int. Conv., Feb. 5, 1914), to Fr. Pat. 465,807, Dec. 6, 1913 (this J., 1914, 643).

THE material is fed over sloping surfaces of refractory material to a point just below the arcs, all the parts of the feeding surfaces being at the same distance, or nearly so, from the pairs of electrodes. Nitrogen gas is passed through the mass from the lower part of the furnace, and the material is subjected to a constant temperature suitable to the formation of nitride.—B. N.

*Hydrogen peroxide; Manufacture of chemically pure solutions of —.* L'Air Liquide (Soc. Anon. pour l'Etude et l'Exploit. des Proc. G. Claude). Fr. Pat. 478,167, July 22, 1914.

IMPURE solutions of hydrogen peroxide are distilled under reduced pressure, and more concentrated solutions are added during the distillation, with the object of increasing the strength of the liquid distillate.—B. N.

*Chlorine water; Manufacture of —.* J. Faust, Cologne. Ger. Pat. 293,724, Oct. 27, 1915.

A CYLINDER with blades or scoops projecting out-

wards from its periphery, rotates within an outer cylinder provided with freely swinging plates attached to its inner wall, so that the blades come in contact with the swinging plates. Chlorine gas and water are introduced separately into the space between the two cylinders, and saturated chlorine water is withdrawn continuously through an outlet.—A. S.

*Silicides of tungsten, molybdenum, zirconium, and other refractory metals; Manufacture of —.* F. Wedekind, Strassburg, and J. Pintsch A.-G., Berlin. Ger. Pat. 294,267, Sept. 12, 1913.

A MIXTURE of the components of the desired silicide, without addition of carbon, is heated at a temperature considerably below the melting point of either component. For example, the hitherto unknown molybdenum silicide, MoSi, may be obtained by heating a mixture of molybdenum and amorphous silicon in an evacuated tube at 1100°–1200° C. It is characterised by its great resistance to acids and other chemical reagents and may be used for the manufacture of incandescence bodies for lighting and heating.—A. S.

*Nitric acid from nitrous gases; Process for the production of —.* A. Foss, Assignor to Norsk Hydro-Elektrisk Kvaestofaktieselskab, Christiania. U.S. Pat. 1,200,334, Oct. 3, 1916. Date of appl., Feb. 23, 1915.

SEE Fr. Pat. 477,726 of 1915; this J., 1916, 601.

*Catalytic reactions; Production of light, voluminous oxide specially suitable for —.* F. Bedford, Sleaford, and E. Erdmann, Halle, Germany, Assignors to The Hydrogenation Co., Cincinnati, Ohio. U.S. Pat. 1,260,696, Oct. 10, 1916. Date of appl., Nov. 12, 1912.

SEE Fr. Pat. 451,155 of 1912; this J., 1913, 602.

*Hydrogen; Process of producing —.* C. Bosch and W. Wild, Assignors to Badische Anilin und Soda Fabrik, Ludwigshafen, Germany. U.S. Pat. 1,200,805, Oct. 10, 1916. Date of appl., Apr. 19, 1913.

SEE Eng. Pat. 27,117 of 1912; this J., 1913, 1108.

*Air; Apparatus for dividing — into its elements by fractional distillation. Method of producing oxygen and nitrogen.* M. Hazard-Flamand, St. Vrain, France. U.S. Pat. 1,201,043 and 1,201,044, Oct. 10, 1916. Dates of appl., Dec. 9, 1908, and Dec. 31, 1915.

SEE Fr. Pat. 394,881 of 1907; this J., 1909, 310.

*Electrolytic cells [for decomposition of water].* Eng. Pat. 191,598. See XI.

*Preparation of tetracupric sulphate and its use as a fungicide.* Addition to Fr. Pat. 476,512. See XIX.

## VIII.—GLASS; CERAMICS.

*Glass; Attack [by reagents] of French, Bohemian, and German —.* P. Nicolardot. Comptes rend., 1916, 163, 355–357.

LABORATORY glassware as now made in France was found equal to the best German (Thuringen and Jena) ware in resisting the action of water (below, at, and above 100° C.), hydrochloric acid, ammonia, and N/10 solutions of ammonium chloride and sodium carbonate. Superior ability to withstand sudden cooling was observed only with Jena and with one make of Bohemian glass. Tables of results and analyses of the various samples examined are given.—F. SODN.

*Glass tubes; New method for the production of accurately dimensioned* —. Lambris. Z. angew. Chem., 1916, 29, 382—383.

THE author has tested burettes, measuring cylinders, apparatus for gas analysis, and other measuring appliances made by K pper's process (Ger. Pat. 262,737; see Eng. Pat. 20,192 of 1913, this J., 1914, 921) and finds that they are accurate to 0.001 mm. The process consists in placing a core, of the same diameter as that desired for the interior of the tube, inside an ordinary glass tube, which is sealed at both ends and evacuated. The tube is then heated externally until it shrinks on to the core and is thereby given the required internal dimensions. The core is then removed, leaving a tube which is so accurate in size and so uniform in diameter throughout its whole length that it may be engraved at once with a scale placed alongside and without the need for calibration, such as is necessary with ordinary tubes.

—A. B. S.

## PATENTS.

*Glass; Method of manufacturing* —. H. I. F. Strandh, Forserum, Sweden. Eng. Pat. 101,685, June 29, 1916 (Appl. No. 9196 of 1916). Under Int. Conv., May 23, 1916.

IN the manufacture of glass, the batch is divided into two or more portions. One portion contains mainly silica and alkali compounds, and carbonaceous matter if alkali sulphates are used. The other contains compounds of calcium and silica, and the portions are admitted separately to facilitate the reduction of the sulphate by the carbonaceous matter and its conversion to silicate. A gas-producing substance, such as calcium carbonate or arsenious acid, may be added to effect agitation of the melting glass mass.—J. E. C.

*Glass; Art of conveying molten* —. K. E. Peiler, Hartford, Conn., Assignor to Hartford-Fairmont Co., Canajoharie, N.Y. U.S. Pat. 1,199,108, Sept. 26, 1916. Date of appl., May 18, 1912. Renewed Feb. 17, 1916.

*Glass-drawing apparatus*. W. L. Clause and R. S. Pease, Assignors to Pittsburgh Plate Glass Co., Pittsburgh, Pa. U.S. Pat. 1,199,763, Oct. 3, 1916. Date of appl., Jan. 23, 1914.

*Glass-melting receptacle*. S. R. Scholes, Pittsburgh, Pa., Assignor to H. C. Fry Glass Co., Rochester, Pa. U.S. Pat. 1,200,889, Oct. 10, 1916. Date of appl., Aug. 31, 1914.

SEE Eng. Pat. 101,393 of 1916; this J., 1916, 1060.

*Gas furnaces*. Eng. Pat. 18,205. See 11b.

*Polariscopes*. Eng. Pat. 14,329. See XXIII.

## IX.—BUILDING MATERIALS.

*Effects of exposure on tar products*. Reeve and Anderton. See III.

*Colour-producing constituents of wood*. Wichelhaus and Lange. See V.

## PATENTS.

*Wood; Preservation of* —. Grubenholzimpregnierung Ges., Berlin. Ger. Pat. 293,890, Apr. 22, 1915.

THE wood is impregnated with aqueous solutions of preservatives, such as metallic salts, alkali fluorides, or compounds of phenols or naphthols, or with fireproofing agents, such as ammonium salts or magnesium compounds, together with trioxymethylene.—A. S.

*Drying bricks, artificial stone, and ores by hot waste gases and hot air; Apparatus for* —. R. Witte, Osnabr ck. Ger. Pat. 294,014, Oct. 18, 1912.

THE dryer consists of a number of parallel chambers or tunnels through which hot waste gases from a furnace are drawn. The outlet flues are arranged transversely across the drying chambers, viz., two, side by side, and separated by dampers or slides, at each end, and one midway between the ends. The outlet flues are each connected independently with all the drying chambers.—A. S.

*Refractory materials; Manufacture of* —. A. Krieger, Ickern. Ger. Pat. 294,021, June 5, 1914.

REFRACTORY materials are obtained by burning a mixture of dolomite with quartz or magnesium silicate in such proportions that the lime combines with the silica whilst the magnesia is left in the free state.—A. S.

*Tar-macadam road material; Production of a binding agent for* —. A. St der, Neuch tel, Switzerland. Ger. Pat. 294,015, July 29, 1914.

A MIXTURE of 15 parts by weight of asphalt mastic, 25 parts of asphalt rock ("crab"), and 10 parts of bitumen is "boiled" for about 2 hours, and 50 parts of tar, which has been heated to 150 C. to expel benzol and light oils, is added, and the mass is well mixed and then worked up in the usual way with stones, etc.—A. S.

*Kilns or ovens for annealing slag bricks or blocks*. T. W. Ridley, Middlesbrough. Eng. Pat. 17,955, Dec. 23, 1915.

*Cement; Process of making coloured* —. J. C. Pelton, San Francisco, Cal. U.S. Pat. 1,200,645, Oct. 10, 1916. Date of appl., June 18, 1914.

SEE Eng. Pat. 18,520 of 1914; this J., 1915, 963.

*Timber; Method of preserving* — from boring organisms. J. E. Cunningham, Sydney, N.S.W. U.S. Pat. 1,201,023, Oct. 10, 1916. Date of appl., Aug. 27, 1914.

SEE Eng. Pat. 784 of 1915; this J., 1915, 1056.

## X.—METALS; METALLURGY, INCLUDING ELECTRO-METALLURGY.

*Mineral industry in South Africa in 1915*. Board of Trade J., Nov. 2, 1916.

THE total value of the mineral output of the Union for 1915 was  43,531,009, as compared with  45,366,224 in 1914. The following table shows the output and value of the chief minerals produced in South Africa in 1914 and 1915:—

Exports of	1914.		1915.	
	Quantity.	Value.	Quantity.	Value.
Gold .. fine oz.	8,398,068	35,664,230	9,096,411	38,649,095
Silver .. "	890,782	102,171	966,177	106,245
Diamonds carats	2,801,917	5,487,194	103,386	399,810
Coal .... tons	8,477,623	2,258,866	8,281,324	2,142,479
Coke .. "	6,493	12,377	7,573	12,360
Copper .. "	29,326	632,355	28,970	1,042,314
Tin .. "	3,429	311,391	3,441	331,450
Asbestos .. "	1,191	20,087	2,133	35,899
Graphite .. "	34	970	41	1,204
Magnesite .. "	572	1,451	627	1,568
Lead .. "	136	1,396	180	1,836
Zinc .... "	—	—	552	2,714
Salt (including by-products) tons	46,290	67,648	45,104	82,089
Lime .. "	66,095	109,041	68,989	110,560
Flint .. "	425	2,508	453	2,327

\* Contained in gold bullion and base metal ores.

There were no new discoveries of minerals of any importance in South Africa in 1915. Small quantities of nickel, mica, iron pyrites, kaolin, and talc were produced during the year. The output of gold in 1915 represented 39.5% of the world's production in that year, as compared with 38% in 1914. All diamond mines were closed down at the outbreak of the war and remained closed during 1915. A few stones, however, were "picked up" on the De Beers' floors.

silver, 754; lead, 1,917,078; copper, 4,560,584; zinc, 8,588,384 kilos.

*Mineral production of the United Kingdom in 1915.*  
[Cd. 8631.]

THE figures given in the subjoined table are taken from Part I. of the Home Office report on Mines and Quarries for 1915, and show the output of minerals from mines, quarries, and brine wells. In addition to these, a production of natural gas amounting to 87,000 cub. ft. is recorded.

Description of mineral.	Mines.		Quarries.*	Total output, 1915.	Total, 1914.
	Coal Mines Act.	Metalliferous Mines Act.			
	Tons.	Tons.	Tons.	Tons.	Tons.
Alum shale	7,911	—	—	7,911	6,078
Antimony ore	—	24	—	24	—
Arsenic	—	2,496	—	2,496	1,988
Arsenical pyrites	—	14	407	421	—
Barium compounds	7,477	53,324	1,676	62,477	48,930
Bauxite	—	11,723	—	11,723	8,286
Bog ore	—	—	1,966	1,966	2,342
Chalk	—	286	3,233,611	3,233,897	4,201,170
Chert, flint, etc.	—	3,033	99,665	102,698	76,213
Chromite	—	—	—	—	100
Clays* and shale	2,068,341	86,202	6,717,278	8,871,821	13,124,361
Coal	253,179,446	—	26,635	253,206,081	265,664,393
Copper ore and copper precipitate	—	746	76	822	2,538
Fluorspar	—	25,377	7,546	32,923	33,816
Gold ore	—	5,086	—	5,086	47
Gravel and sand	—	10,669	2,339,568	2,350,237	2,498,872
Gypsum	—	204,574	42,655	247,229	265,365
Igneous rocks	79	43,010	6,042,326	6,085,415	7,135,243
Iron ore	6,080,218	1,795,887	6,358,907	14,235,012	14,745,828
Iron pyrites	9,255	1,280	—	10,535	11,654
Lead ore	—	20,698	46	20,744	26,013
Lignite	—	1,783	10,828,229	11,115,909	12,180,015
Limestone (other than chalk)	4,464	283,216	—	4,640	3,437
Manganese ore	—	4,640	—	4,640	11,089
Ochre, amber, etc.	—	4,030	4,959	8,989	3,268,608
Oil shale	2,998,652	—	—	2,998,652	189,905
Rock salt	—	131,348	—	131,348	1,870,994
Salt from brine	—	—	1,874,257	1,874,257	8,464,538
Sandstone	141,420	57,626	2,321,610	2,520,656	318,012
Slate	—	48,893	177,144	226,037	180
Soapstone	—	750	100	850	13,157
Sulphate of strontia	—	—	640	640	8,085
Tin ore (dressed)	—	6,427	1,717	8,144	205
Tinmen ores	—	327	4	331	344
Uranium ore	—	82	—	82	13,419
Zinc ore	—	12,087	—	12,087	—
Total	264,497,263	2,815,816†	40,081,242	307,394,321‡	329,207,583

\* Exclusive of the produce of most of the quarries less than 20 feet deep, but including the produce of all open workings for iron ore, bog ore, ochre, sulphate of strontia, and tin ore, etc.  
† Including china clay, china stone, and mica clay.

#### Mineral output of Sweden.

THE official report of Swedish mineral production shows the following, in metric tons:

	1914.	1915.
Iron ore	6,586,630	6,883,308
Coal	368,639	412,261
Gold ore	639	221
Silver-lead ore	3,100	2,671
Molybdenite	7	37
Copper ore	8,539	10,549
Manganese ore	3,843	7,807
Zinc ore	42,279	55,937
Nickel ore	156	1,692
Pyrites	33,313	76,324
Feldspar	20,818	12,105
Quartz	36,128	33,818
Graphite	56	87
Powdered pyrolusite	81	126

The production of iron ore from the Kiruna-Vara deposits was reduced from 2,728,363 tons in 1914 to 2,076,512 tons in 1915, owing to the difficulties of shipping from Narvik on account of the war. The electrolytic production of zinc at Trollhättan was increased from 2,299,761 kilos. in 1914 to 8,588,384 kilos. in 1915. The metal production, with the exception of iron, was: Gold, 37 kilos.;

*Commercial sheet iron; Atmospheric corrosion of —, with special reference to the influence of copper and mill scale.* E. A. and L. T. Richardson. Amer. Electrochem. Soc., Sept., 1916. Met. and Chem. Eng., 1916, 15, 450—453. (See also this J., 1915, 83.)

THE investigation was made on commercial sheets (26 gauge) of Bessemer steel (Cu trace, Mn 0.300%), open-hearth steel (Cu trace, Mn 0.413%), charcoal iron (Cu 0.044, Mn 0.031%), commercially pure iron (Cu 0.016 and 0.028, Mn 0.028 and 0.009% respectively), copper-bearing iron (Cu 0.237, Mn 0.006%), copper-bearing steel (Cu 0.181, Mn 0.100%), copper-bearing Bessemer steel (Cu 0.256, Mn 0.315%), and copper-bearing open-hearth steel (Cu 0.268, Mn 0.387%), which were used in the "black" condition as received and after annealing and removing the mill scale by pickling in sulphuric acid and scouring with fine emery. Test-pieces of the same size were exposed to the atmosphere until failure was indicated by the sheet being in such condition that perforation was observed on removing the rust by gentle tapping with a file. The copper-bearing steels were found to be decidedly superior to pure iron, ordinary steel, or charcoal iron, and the corrodibility of pure iron to be decreased to a much smaller extent than

that of steel by the addition of similar amounts of copper. Charcoal iron behaved similarly to pure iron, and both were superior to ordinary steel. Mill scale stimulated corrosion in rapidly rusting steels and retarded it in slowly rusting materials. The relative incorrodibility of copper-bearing steels is believed to be due to some mutual influence of manganese and copper, and the addition of larger amounts of these metals, with chromium, vanadium, tungsten, and molybdenum, is suggested as a possible means of increasing the resistance of iron and steel to atmospheric corrosion.—W. E. F. P.

**Ferrosilicons; Poisonous gases from commercial** — N. S. Kurnakoff and G. G. Urasoff. *Gorny J.*, 1914, 159—204. *Z. angew. Chem.*, 1916, 29, Ref., 458. (See also Pellet, this J., 1914, 774.)

ON cooling molten iron-silicon alloys containing from 33.4 to 100% Si, a solid phase ("Lebeauite") of varying composition crystallises out at 1243°—1245° C.; when aluminium and phosphorus are present, ternary or quaternary solid solutions are formed. The ternary systems (Fe-Si-P and Fe-Si-Al) are not affected by water, but the quaternary solid solutions containing both phosphorus and aluminium are decomposed by water with evolution of hydrogen phosphide, and disintegrate when exposed to the air. The evolution of poisonous gases from commercial ferrosilicon containing 33.4—100% Si is attributed to the presence of this unstable quaternary solid solution. In alloys of lower silicon content, phosphorus (up to 1.7%) and aluminium (up to 3%) occur as constituents of the  $\gamma$ -solid solution of silicon in iron, and only insignificant quantities of hydrogen phosphide are produced from such alloys. Calcium phosphide is not soluble in either liquid or solid ferrosilicon, and the quantity of hydrogen phosphide evolved from commercial ferrosilicon is always considerably greater than corresponds to the calcium content of the alloy.—A. S.

**Copper deposits discovered in Newfoundland; New** — U.S. Commerce Reports, Oct. 20, 1916.

THE discovery of important copper deposits at Little Bay, about 200 miles north of St. John's, Newfoundland, has been reported. The lode is known at present to be 300 ft. wide, and there are veins, 1—2 ft. wide, containing nearly pure cuproprites with up to 29.5% Cu. The working of the deposit has already begun, and hydraulic plant is being installed for operating a 200-ton concentrator.

**Blast v. reverberatory furnace [for copper-gold ores].** B. Magnus. *Eng. and Min. J.*, 1916, 102, 668—669.

ESTIMATES of the cost of treatment of the copper-gold ore of Mount Morgan, Australia, in blast-furnaces and in reverberatory furnaces, showed only slight differences in profits, but operating considerations and known results turned the balance in favour of blast-furnace treatment, which has been adopted.

**Zinc; Comments and speculations on the metallurgy of** — W. R. Ingalls. *Eng. and Min. J.*, 1916, 102, 621—624.

IN a critical discussion of the details of zinc metallurgy, the conditions affecting hydro-electrolytic methods of production are considered in conjunction with the recovery of residual zinc from the leached ore by direct smelting in the electric furnace or "burning" on Wetherill or mechanical grates and collecting the resulting fume of zinc oxide in a bag-house or by the Cottrell system of electrical precipitation. The relative merits of the various types of furnace in use or proposed for roasting and distillation are

also discussed, together with the probable advantages of vertical retorts and pre-reduction of the charge before distillation. In view of the increasing production of zinc concentrates by flotation, the problem of briquetting excessively fine ore for smelting is likely to become urgent in the near future.—W. E. F. P.

**Zinc dust; Electrolytic** — H. J. Morgan and O. C. Ralston. U.S. Bureau of Mines. *Amer. Electrochem. Soc.*, Sept. 28, 1916. *Met. and Chem. Eng.*, 1916, 15, 465—468.

By electrolysing aqueous solutions of zinc salts under various conditions, deposits of spongy zinc were obtained which crumbled into "zinc dust" on drying. The spongy metal deposited from solutions of zinc sulphate and chloride was more or less satisfactory; but the best product was obtained by electrolysing, at 5 volts, a solution of sodium zincate, prepared by saturating a 30% solution of sodium hydroxide with zinc oxide, and maintaining the zinc content of the bath by the addition of zinc oxide or by the use of zinc anodes. The average current efficiency in the deposition of spongy zinc by this method was about 60%, the power required was somewhat less than 3 kilowatt-hours per lb. of zinc dust. The efficiency of the latter as a precipitant for gold and silver in cyanide solutions (determined by Sharwood's silver cyanide method; this J., 1912, 437) was 74% as compared with 45% for the average grade of European zinc dust.—W. E. F. P.

**Lead-smelting practice in the United States.** A. S. Dwight. *Eng. and Min. J.*, 1916, 102, 671—677.

RECENT progress in lead smelting has been practically confined to the preparation and handling of the different components of the furnace charge with a view to effecting economy in labour and improvement in furnace operation. The essential features of the lead blast furnace have undergone no appreciable change during the last decade. A typical, modern, rectangular blast furnace will smelt about 250 short tons of charge per 24 hours (or about 4.5 tons per sq. ft. of area at the tuyeres), the blast pressure being 30—40 oz., and the charge containing the fuel equivalent of 10—11% of fixed carbon, plus 3% of sulphur. A satisfactory roasting process for lead smelting should effect a maximum elimination of sulphur and leave the product in coarse form. The sulphur content of raw ore is readily and economically reduced to 10% in the old style of mechanically-ribbled roasting hearth; but the finishing roast is best effected in Huntington and Heberlein pots or on Dwight and Lloyd sintering machines, by means of which a coarse product (containing 2.5—5% S) in excellent condition for smelting is obtained. By the development of these modern roasting methods, hand roasting has been rendered practically obsolete, and modern American practice is based on the use of one or other of these systems for the desulphurisation and agglomeration of all ore fines. A charge for sintering should contain not more than 16—18% S, and, to ensure regular fusion, should be so compounded that the sulphide particles are in contact with others of a more refractory nature. In some plants the Dwight and Lloyd and/or the Huntington and Heberlein systems are used for initial and finishing roasting, but two operations are always necessary to effect a sufficient reduction of the sulphur content; sintered products containing as little as 2.5% S have been recently obtained from raw ore by the employment of automatic apparatus in conjunction with this method of "double roasting." The old Scotch hearth, formerly used to a considerable extent in lead smelting but practically superseded by modern roasting methods, has been recently

revived in modified form by W. E. Newnam and successfully employed in the treatment of rich lead concentrates.—W. E. F. P.

*Lead from brine leaches; Electrolytic recovery of* — C. E. Sims and O. C. Ralston, Amer. Electrochem. Soc., Sept., 1916. *Met. and Chem. Eng.*, 1916, 15, 410—415.

EXPERIMENTS have been made on the electrolysis of lead compounds, such as the sulphate and chloride, in brine solutions, and, considering the cheapness of the leaching agent, the high electrochemical equivalent of lead, and the high efficiencies possible, it appears that a metal of low value, such as lead, may be profitably electrolysed. Applied to mill tailings or a mine dump, a fair profit might be made, but a 10% material could not be profitably worked with a mining charge of several dollars per ton added to the cost, although a lead carbonate deposit near the surface could stand a fairly considerable mining charge if a 15 to 20% ore were available. It is stated that the method will be found applicable to ores, such as many of the carbonate ores, obtained at points distant from lead smelters, too low in grade to ship and refusing to yield to gravity concentration. —B. N.

*Mercury ores; The smelting of* — W. H. Landers. *Eng. and Min. J.*, 1916, 102, 630—633.

LITTLE progress has been made in the metallurgy of mercury since the introduction, in 1876, of the Scott tile furnace which is still the standard type for the reduction of cinnabar ores; but in view of the diminishing mercury content of the ores now mined in the U.S.A. (less than 1% on the average during the last 5 years), wet concentration is becoming more general. Continuous furnaces of several types, generally operated on the lime-kiln principle, are still employed with satisfactory results in the treatment of coarse ore, suggesting the practicability of briquetting the finer ores or concentrates as a preliminary to similar treatment. Briquetting has been unsuccessful hitherto, owing to the lack of a suitable binding material. The binder should be free from substances which evolve hydrocarbon vapours on heating, since these cause trouble in the collection of mercury from the condensing system; the use of oil fuel in mercury furnaces is attended by a similar difficulty, and the best results in all types of furnaces have been obtained hitherto by the use of wood fuel. The method of reduction in retorts is still practised and will be probably further developed in the treatment of rich products from wet concentrating mills. The use of multiple-hearth roasting furnaces for the treatment of cinnabar concentrates has scarcely yet passed the experimental stage, but these furnaces have proved more economical than the Scott type in fuel consumption, and by reason of their lower first cost and greater facilities for control are likely to be still further developed. Owing to the high losses of mercury occurring in the tile furnace method of treatment (20% on comparatively high-grade, coarse ore, and up to 40% on low-grade, fine ore), a wet process of extraction is desirable; and in the author's opinion future developments will either take this course or result in the improvement of wet concentration until extractions exceeding 90% are possible on the commercial scale.—W. E. F. P.

*Mercury; Freezing point of* — R. M. Wilhelm. U.S. Bureau of Standards. *Scient. Paper* No. 294. *J. Franklin Inst.*, 1916, 182, 525.

USING platinum resistance thermometers, calibrated at 0° C., 100° C., and 444.6° C. (b.pt. of sulphur), the value —38.87° C. was found for the freezing point of mercury. This is in very good

agreement with the value, —38.89° C., obtained by Henning in 1913 at the Reichsanstalt, Germany.—B. V. S.

*Bismuth; Pure* — F. Mylius and E. Groschuff. *Z. anorg. Chem.*, 1916, 96, 237—264. *Z. angew. Chem.*, 1916, 29, Ref., 458.

COMMERCIAL samples of reputedly pure bismuth all contained silver, lead, and copper; tin, nickel, zinc, and platinum were also present in certain cases. Samples of electrolytic bismuth contained platinum and silver and traces of lead, copper, and zinc. The best method of purification was found to be crystallisation of normal bismuth nitrate from acid aqueous solution and of the metal from the fused impure metal. The melting point of the purest bismuth obtained was 271° C., and the electrical resistance of pure bismuth wire was 1.20 ohms.—A. S.

*Secondary metals in the United States in 1915.*

ACCORDING to a report by J. P. Dunlop, of the United States Geological Survey, on the production of secondary copper, zinc, lead, tin, antimony, and aluminium from scrap metal, sweepings, skimmings, and drosses, the total value of the recovery amounted to more than \$114,000,000, exclusive of the value of old iron, steel, platinum, nickel, gold, silver, and other metals.

Assuming that remelted brass had an average content of 70% copper, the total recovery of secondary copper was 196,187 tons, of which 29,787 tons was recovered by plants treating primary metals and the balance by plants treating only secondary materials. Secondary lead recovered in 1915 amounted to 78,900 tons. The total increase over 1914 was about 17,800 tons, and that of lead in alloys more than 10,700 tons. Secondary zinc, including that in brass, amounted to 92,575 tons in 1915; being equal to 16% of the production of primary spelter in the United States. Secondary antimony production increased from 2646 short tons in 1914 to 3102 tons in 1915, all but two tons being recovered in alloys. Secondary tin recovered in 1915 was equal to about 24% of imports as metal or oxide, being 13,650 tons as compared with 12,447 tons in 1914. The metal recovered as tin was 5250 tons and that in alloys and chemical compounds, 8400 tons. The latter includes the tin content of products made from clean tinplate scrap, consisting mainly of tin chloride with some oxide, etc. Secondary aluminium recovery in 1915 amounted to 8500 tons, as compared with 4522 tons in 1914. Of this 2800 tons was recovered in alloys, mainly of 92% aluminium and 8% copper. The increase in quantity of secondary aluminium in 1915 is said to be due to the use of old castings in automobile manufacture.

*Flotation [of ores]; Laboratory experiments on the* — C. Y. Clayton. *Bull. School of Mines and Met., Univ. of Missouri*. Vol. 3, No. 1. Aug., 1916. 40 pages.

EXPERIMENTS were undertaken to compare the value of different oils for flotation purposes under the same conditions. Those oils which are more or less miscible with water (e.g., essential and pine oils, cresol, wood creosote) seem to be the best in regard to frothing properties; those that give an ephemeral, small-bubble froth yield a cleaner concentrate than oils which form a thick stiff froth (e.g., fixed oils, coal tar, wood tar) though in the latter case the recovery may be greater. To get a clean concentrate it may therefore be necessary to sacrifice recovery, and vice versa. With a low-grade dolomitic lead ore, coal-tar creosote gave the purest concentrate (Pb 74%), oil of cloves giving the highest extrac-

tion. With a zinc slime (Zn 1.75%) pine oil gave a 50% concentrate, a mixture of creosote and refined tar a 46% product. Oils giving good flotation results were found to have a high dielectric constant. As the quantity of added oil increased above a certain quantity, the purity and quantity of concentrate decreased. The flotation concentrates submitted to screen analysis showed the largest proportion of gangue in the finest material.—W. R. S.

*New method for measuring resistivity of molten materials. Results for certain alloys.* Northrup and Sherwood. See XI.

*High temperature heat developed during electrolysis.* Iiering. See XI.

#### PATENTS.

*Roasting furnaces; Mechanical.*—A. Zavelberg, Hohenlohehütte, Germany. Eng. Pat. 12,708. Sept. 4, 1915.

The air which is circulated through the hollow rake-arms and rakes to cool them, is discharged through outlet ports, inclined downwards, in the rear faces of the rakes, thus coming directly in contact with material which has been broken up by the rakes.—A. S.

*Cupolas and other shaft furnaces.* J. A. Parsons, Johannesburg, Transvaal. Eng. Pat. 14,205, Oct. 7, 1915.

A TUBULAR air-blast heater forms a continuation of the furnace stack above the charging floor, and comprises upper and lower headers connected by vertical heating pipes, with baffles between the wall of the stack and the pipes. The air enters through the upper header, and the lower header communicates with down-take pipes connected with corresponding tuyères.—W. R. S.

*Tin from tinned iron-scrap; Process of separating and removing all the—* P. Marino, London. Eng. Pat. 14,231, Oct. 7, 1915.

The scrap is treated with a solution of an alkali bichromate in hydrochloric acid.—W. R. S.

*Soldering of aluminium or aluminium alloys.* W. Overend, H. G. Grinlinton, and Overend Aluminium Soldering Processes, Ltd., Auckland, N.Z. Eng. Pat. 17,118, Dec. 6, 1915.

The surface of the aluminium is prepared, prior to soldering, by heating it and applying a flux of stearic acid and then an alloy of tin and zinc. The temperature is raised to melt the alloy, and the heating maintained whilst the surface of the aluminium is gently rubbed by a special tool comprising a strip of zinc. The molten alloy is distributed, and the coating of oxide on the surface of the aluminium is acted upon by the tool, thus causing the oxide to separate from the metal and mix with the molten alloy. The action is carried on at, or above, the temperature at which the zinc is melted, and the surface of the aluminium becomes covered or alloyed with a coating consisting practically wholly of tin, the surplus alloy being wiped off. The heating of the coated aluminium is continued, and an alloy of tin and cadmium applied, using stearic acid as a flux. The prepared surfaces, covered with the alloy of tin and cadmium, are then soldered or sweated together, with the use of stearic acid as a flux.—B. N.

*Oil flotation; Process of and apparatus for the separation of metalliferous particles by—* Metallurgical Co. of America, New York. Assignees of D. F. Haley, Wallace, Idaho, U.S.A. Eng. Pat. 100,637, May 9, 1916 (Appl. No. 6658 of 1916). Under Int. Conv., June 4, 1915.

The ore pulp is mixed with oil, or oil and air, and discharged downwards in the form of a jet

of high velocity on to the surface of a confined body of liquid of relatively small volume, so as to aerate the pulp and form a froth as a result of the splashing action. The froth and liquid overflow into a flotation box where the froth is skimmed off by a slowly rotating scraper. The colloidal and slimy gangue matter just below the froth is removed separately through an adjustable outlet; the tailings are discharged through a valved outlet at the bottom of the box.—W. R. S.

*Ingot and castings; Production of—* Sir W. G. Armstrong, Whitworth and Co., Ltd., Newcastle-upon-Tyne, E. F. Law, Manchester, and C. P. Sandberg, London. Eng. Pat. 101,650, Feb. 7, 1916. (Appl. No. 1810 of 1916.)

In order to keep the ingot molten and prevent piping, blowholes, and segregation, the mould is provided at the bottom with a loose electrical contact device, and an arc is produced between the top of the casting and an electrode above it.—W. R. S.

*Silver and gold; Extraction of silver, or— from ores.* J. Y. Johnson, London. From M. H. Caron, Weltevreden, Java. Eng. Pat. 101,665, Apr. 10, 1916. (Appl. No. 5219 of 1916.)

SILVER or gold ores containing manganese dioxides are subjected to a reducing roast preparatory to amalgamation or cyaniding.—W. R. S.

*Heat treatment [of metals].* W. J. Wrighton, Philadelphia, U.S.A. Eng. Pat. 100,679, May 3, 1916. (Appl. No. 6350 of 1916.) Under Int. Conv., June 15, 1915.

A THERMO-COUPLE or other heat-responsive device is placed within the furnace chamber in which the metal is heated, not necessarily in contact with the metal, and a temperature-time curve is plotted. The critical range of the metal is indicated by abrupt changes in the direction of the curve. It is thus possible to control processes of heat treatment involving the heating of the metal to or above the critical range, and the "soaking" operation may be omitted. The process is based on the fact that although the thermo-couple, even if in direct contact with the outer surface of the metal, does not register the true temperature of the metal unless the latter be kept at a given temperature for a considerable time, yet the critical point or range occurs at the same time on the temperature-time curve of the external thermo-couple as on the corresponding curve of a thermo-couple placed at any point within the mass of metal. The thermo-couple need not be calibrated.—A. S.

*Zinc; Process for separating— from alloys containing it.* G. Heinecker, Breslau. Ger. Pat. 294,287, Feb. 5, 1916.

THE alloy is melted in a pot placed in the upper part of a furnace. In the bottom of the pot is an opening which is alternately opened and closed, the molten metal flowing through the opening in rapid succession, by a valve. The molten alloy flows through the opening and through a short connecting tube and is discharged into a retort in the lower part of the furnace. The zinc is volatilised in this retort and the vapour passes to a condenser.—A. S.

*Classifier and dewaterer.* W. J. Boudwin, Assignor to The General Engineering Co., Salt Lake City, Utah. U.S. Pat. 1,201,014, Oct. 10, 1916. Date of appl., July 22, 1916.

*Ore-concentrating apparatus.* T. A. Janney, Garfield, Utah. U.S. Pat. 1,201,053, Oct. 10, 1916. Date of appl., Apr. 23, 1914.

*Simultaneous purification, desiccation, and concentration of [blast-furnace] gases.* Fr. Pat. 478,260. See 11A.

*Apparatus for drying bricks, artificial stone, and ores by hot waste gases and hot air.* Ger. Pat. 294,014. See 1X.

## XL—ELECTRO-CHEMISTRY.

*Molten materials; New method for measuring resistivity of —. Results for certain alloys.* E. F. Northrup and R. G. Sherwood. J. Franklin Inst., 1916, 182, 477—509.

A DESCRIPTION is given of two types of a "resistometer" which is inserted directly into a considerable mass of the molten material whose resistivity it is desired to measure. Tungsten or molybdenum wires are used both for current and potential terminals. The latter, which serve for measuring potential drop when current is passed through the "resistometer," are arranged so that the distance between the points is constant. The cross-section and length of the fluid-column of which the resistance is measured are thus made invariant. The constant of the "resistometer" is obtained by measuring the resistance when pure mercury is taken. The temperature of the column is measured by a thermo-couple. Alternating current must be used for the measuring current to avoid difficulties arising from parasitic electromotive forces and currents. These become so large and erratic above 500° C. that accurate measurements become exceedingly difficult when direct current is used as the measuring current. A specially designed alternating-current galvanometer is used, and resistivity readings are made directly in microhms per cm. cube with a Kelvin double-bridge. Resistivity-temperature curves for several metals and alloys are given, a common characteristic being their linear character for the molten materials. The curves obtained with different bismuth-tin alloys in the molten state have approximately the same slope, and a linear relation exists between the resistivity of these alloys and the percentage of grm.-atoms of each constituent.—T. St.

*Electrical conductivity; Chemical composition versus —.* C. G. Fink. Amer. Chem. Soc., Sept. 28, 1916. Met. and Chem. Eng., 1916, 15, 464—465.

FROM observations made on a black metal powder (tungsten), a white insulator powder (thoria), and mixtures of these, which were pressed into rods and heated to 1600° C. in a "tungsten hydrogen furnace," it is concluded that the electrical conductivity of a substance is dependent upon the shape and distribution of the component grains or particles and upon the presence or absence of thin films of secondary material enveloping such grains. On this basis the comparatively high conductivity of gels containing only a trace of conducting material is explicable; and also the marked difference in resistance between, for example, two samples of commercial copper of identical composition but having the impurity uniformly dissolved in one case, and forming a film ("cement") around the grains of the pure metal in the other. The high resistance of such films of copper sulphide, oxide, or arsenide would account for the high resistivity of copper containing only traces of these impurities.—W. E. F. P.

*High temperature heat developed during electrolysis.* C. Hering. Amer. Electrochem. Soc., Sept., 1916. Met. and Chem. Eng., 1916, 15, 454—455.

WHEN the current density on a cathode immersed

in certain aqueous electrolytes is increased sufficiently, the cathode becomes red hot and may even melt. In the present experiments a lead anode was employed with a small cathode of thin sheet iron in an electrolyte of dilute sulphuric acid (sp.gr. 1.2), the cathode being gradually raised until the high temperature effect was produced and then slowly lowered again in the electrolyte. The high temperature condition was found to persist for a depth considerably greater than that at which it was first produced during the raising of the electrode. The red-hot period was succeeded by a stage in which the cathode was enveloped by a blue, hissing film which, as the lowering proceeded, broke suddenly, thus causing the surface of the cathode to be again wetted and the normal conditions of electrolysis to be restored. During the heating period, globules of black, brittle material were formed on the cathode—presumably black iron oxide formed by transference of oxygen across the gas film through which the passage of the current appeared to take place by arcing. The surface energy developed on the cathode during the first and second stages of heating and at the final breaking of the film amounted to about 370, 250, and 120 kw. per sq. ft. respectively; 370 kw. represents a rate of surface heating about 440 times that obtained in ordinary boiler practice, and is much higher than that obtainable by a blast flame. The surface hardening of steel objects by this method, although impracticable at the voltages used (up to 120) owing to oxidation, might be possible with more rapid heating at higher voltages; and the method might be employed, for example, in alloying a metal surface with another metal plated upon it.—W. E. F. P.

*Chemical reactions under the influence of the electric discharge in an atmosphere of an inert gas.* F. Skaupy. Ber., 1916, 49, 2005—2006.

IT has previously been shown that a separation of the components of gaseous mixtures can be effected by means of a direct current in a discharge tube (this J., 1916, 1068), and it is now found that by similar means the components of dissociable gaseous compounds, such as aluminium chloride, can be completely separated and either deposited or led off from the neighbourhood of the electrodes. By carrying out the discharge in an atmosphere of an inert gas, such as helium or argon, lower potentials can be employed, and the electrodes can be protected from the action of the reacting materials by restricting the latter to the middle portion of the discharge tube, and separating the reaction products, e.g., by condensation, before they reach the electrodes. By a further application of the method certain reactions can be brought about under the influence of the discharge, either direct or alternating. Thus if hydrocarbon vapours are led into the tube, polymerisation, without any trace of carbonisation, occurs with considerable reaction velocity, and carbon-containing gases or vapours mixed with nitrogen are converted into organic nitrogen compounds.—G. F. M.

## PATENTS.

*Electrolytic cells [for decomposition of water].* C. Churchill and Co., Ltd., London, and E. Geeraerd, Oldham, Lancs. Eng. Pat. 101,598, May 11, 1916. (Appl. No. 6735 of 1916.)

THE sides of the cell are used as electrodes, and, in place of a diaphragm, two series of superimposed vanes of non-conducting material are placed close to, but not necessarily touching, the faces of the respective electrodes, and are inclined thereto at a suitable angle in order to deflect the



gas towards the electrode at which it was liberated. The gas passes either through the narrow passages between the extremities of the vanes and the electrode, or through vertical grooves in the electrode to the respective receivers for the hydrogen and oxygen.—B. N.

**Ozone;** [Electrical] apparatus for producing —. J. Steynis. Fr. Pat. 478,133, July 17, 1914.

CONDENSATION of moisture on a high-tension apparatus for the production of ozone is prevented by enclosing the generator, the refrigerating apparatus for drying the air to be ozonised, and the transformer in an air-tight, heat-insulated chamber filled with dry air. The movable electrodes and dielectrics may be removed from the generator, without removing them from the chamber.—B. N.

**Furnaces; Method and apparatus for treating materials in electric** —. Soc. Anon. Métallurgique "Procédés de Laval." Fr. Pat. 478,940, June 7, 1915.

SEE U.S. Pat. 1,196,202 of 1916; this J., 1916, 1068.

**Electric furnaces; Treatment of materials in** —. Soc. Anon. Métallurgique "Procédés de Laval." Fr. Pat. 478,941, June 7, 1915.

SEE U.S. Pat. 1,160,244 of 1915; this J., 1916, 259.

**Production of cuprous oxide electrolytically.** Eng. Pat. 14,310. See VII.

**Preparation of aluminium nitride in electric arc furnaces.** Addition to Fr. Pat. 465,807. See VII.

**Electrolytic manufacture of caustic potash.** Fr. Pat. 478,371. See VII.

## XII.—FATS; OILS; WAXES.

**Ray liver oils.** M. Tsujimoto, Kōgyō-Kwakaku-Zasshi (J. Chem. Ind., Tokyo), 1916, 19, 833-811.

Oils extracted from the livers of five species of Japanese rays gave the following values:—

	Emilia fish, <i>Rhinobatus schlegelii</i> .	Common ray, <i>Raja leucoraja</i> .	"Uchiwa zané," <i>Discodolus sinensis</i> .	Sting ray, <i>Dasyatis akagi</i> .	Eagle ray, <i>M. diabolus labridi</i> .
Sp.gr. at 15°/4° C.	0.9267	0.9329	0.9324	0.9216	0.9203
Acid value	2.66	2.02	2.36	1.47	9.83
Saponif. value	182.81	182.69	179.59	185.10	175.18
Iodine value (Wijs)	183.67	209.06	192.54	184.60	136.08
Ref. index at 20° C.	1.4825	1.4843	1.4826	1.4827	1.4773
Butyrefractometer, 20° C.	87.3	90.4	87.5	87.6	78.2
Unsaponif. matter, per cent.	3.15	3.11	2.60	2.94	4.47
Melting pt. of fatty acids, °C.	34-35	23-29	—	34-35	above 37
Polybromides of fatty acids, per cent.	60-20	65-23	62.96	63.08	33.51
Br content of polybromides, per cent.	70-53	69.97	70.36	70.73	68.87

The polybromides (insoluble in ether) turned black and decomposed above 200° C. The unsaponifiable matters were crystalline and semi-solid. They contained cholesterol, but were free from the liquid hydrocarbon found in shark oils (this J., 1916, 609, 1121). The characters of the liver oils from the common ray, "uchiwa-zané," and from the sting-ray resemble those of shark liver oils of high sp.gr., such as the liver oils of the dog shark, hammer-headed shark, and angel-fish.—C. A. M.

**Oils and fats; Relation between the most important physical and chemical constants of** —. H. J. Backer. Chem. Weekblad, 1916, 13, 954-967. J. Chem. Soc., 1916, 110, ii, 543.

For oils and fats composed solely of mixtures of glyceryl esters of saturated and unsaturated mono-carboxylic acids, the relation between the refractive index ( $n$ ), the density ( $d$ ), the saponifi-

cation value ( $V$ ), and the iodine value ( $I$ ) is given by the expression:

$$(n_D^{20}-1)/(n_D^{20}+2) \times 100/d_4^{20} =$$

$$33.07 + 0.00075I - 0.01375V + 0.002(I-15).$$

Extracted soya meal poisoning. See XIXA.

## PATENTS.

**Glycerides; Process of saponifying** —. Process of producing fatty acids and manufacture of soap and candles therefrom. S. G. S. Dicker, London. From The Reuter Process Co., Chicago, U.S.A. Eng. Pats. (A) 9393 and (N) 9394, June 26, 1915.

(A) The glycerides are fractionally saponified by boiling with sulphonic acids, such as Twitchell's reagent (Eng. Pat. 471 of 1898; this J., 1898, 588), the discoloured fatty acids being removed after each stage, and only the watery portion returned to the saponifying vessel for the next boiling. In this way a much whiter product is obtained. (B) The process claimed in (A) is adapted to the production of fatty acids in accordance with Eng. Pat. 10,199 of 1913 (this J., 1914, 603). Saponification is effected by means of an organic catalyst in the absence of air, while impurities are removed between the successive boilings. Soap, candles, etc., made from the resulting fatty acids are not discoloured by exposure to air and sunlight for 10 days.—C. A. M.

**Catalysts [for hydrogenating oils]; Preparation of** —. E. B. Higgins, Liverpool. Eng. Pat. 21,041, Sept. 17, 1913.

Fatty acid salts of nickel, cobalt, iron, or copper are heated in an inert medium, such as a fatty oil, until the mass blackens. The process is preferably carried out in a vessel from which air is excluded, e.g., by passing a stream of a gas such as nitrogen or carbon dioxide through the mixture.—C. A. M.

**Fish oils; Process for deodorising** —. G. Weiss, Ulchenbach. Ger. Pat. 294,136, June 5, 1913.

The oil is heated at about 200° C. at atmospheric pressure and subsequently treated with steam

in the presence of basic substances, especially oxides or hydroxides of alkali, alkaline-earth, or other metals. The deodorised oils are not darker in colour than the original oils.—A. S.

**Process for preventing flocculation of calcium soaps in washing baths.** Ger. Pat. 294,028. See VI.

## XIII.—PAINTS; PIGMENTS; VARNISHES; RESINS.

**Resin [from wood pulp waste lyes]; Liquid Swedish** —. K. Lorentz. Seifensieder-Zeit., 1916, 43, 501-502. Z. angew. Chem., 1916, 29, Ref., 445.

The liquid resin obtained from wood pulp waste lyes by treatment with acid was formerly a waste product, but cannot now be obtained at a lower

price than M.90 per 100 kilos. (about 4½d. per lb.). The resin obtained from sulphate-cellulose waste lyes is light brown, but gradually darkens on exposure to air until ultimately it becomes black. It has an unpleasant odour and has no drying properties. It contains fatty acids, a yellow colouring matter, and resins, and may be used in soap manufacture. The resin from sulphite-pulp waste lyes has a high sulphur content. It has an unpleasant odour, but, unlike that from sulphate lyes, is soluble in water and has drying properties. It is not suitable for soap manufacture, but may find application in the varnish industry and in the manufacture of adhesives. The crude resin may be refined by distillation, by boiling with sulphuric acid or with a strong solution of sodium chloride and milk of lime, or by saponification. Bleaching is best effected with bleaching powder. The crude resin may be used in the preparation of wagon-grease, lubricants for driving belts, and bird-lime.—A. S.

*The resin of coniferous woods, and deresinification of wood pulp.* Sieber. See V.

#### PATENTS.

*Coloured lime and process of producing same.* G. I. Keck, Springfield, Ohio, U.S.A. Eng. Pat. 101,514, Apr. 13, 1916. (Appl. No. 5425 of 1916.)

QUICKLIME is slaked with a quantity of coloured water sufficient to hydrate the lime and leave it as a dry, uniformly coloured powder suitable for wall paints, etc., or the quicklime may be mixed with colouring matter before the addition of the water.—C. A. M.

*Zinc white; Process of manufacturing*—. T. Seirensho, Ltd. Fr. Pat. 479,614, Aug. 28, 1915.

ZINC hydroxide is precipitated from an aqueous solution of zinc sulphate by means of milk of lime, in presence of sodium sulphate or a mixture of sodium sulphate with chlorides, and the precipitate is filtered off while the calcium sulphate still remains in the form of a supersaturated solution, and is subsequently converted into zinc white.—C. A. M.

*Ultramarine; Manufacture of*—. Gebr. Vossen, Aachen, and L. Bock, Bad Homburg-Kirchhof. Ger. Pat. 293,310, Mar. 25, 1915.

SULPHUR contaminated with tar, as obtained from spent oxide from gas purification by extraction, distillation, or the like, is used in the manufacture of ultramarine.—A. S.

*Condensation products [from phenols and formaldehyde] and method of manufacturing a substance capable of replacing ivory, mother of pearl, celluloid, etc., and its applications in dentistry and industry.* L. Eilertsen. Fr. Pat. 478,884, May 13, 1914.

PHENOLS or their homologues are fused with a substance capable of yielding formaldehyde (trioxymethylene), 1 to 10% of a base (soda solution) is added, and then an acid to effect the final condensation, which takes place without elimination of water or separation of the constituents. The use of phosphoric acid, alone or in admixture with other acids, gives a white translucent product, while alcohols and esters (notably amyl alcohol and amyl acetate) insoluble in water but capable of dissolving the product, may be introduced to increase the transparency. Colouring matters may also be incorporated. The product may be moulded, with or without pressure, and in dentistry may be used for artificial teeth and plates, and for stopping teeth.—C. A. M.

*Phenols and aldehydes; Condensation product from*—. W. Reeser. Fr. Pat. 479,319, July 20, 1915. Under Int. Conv., July 28, 1914.

CONDENSATION products are prepared from a mixture of oils or fats with aldehydes and phenols, which is treated with alkali in about twice the proportion required to saponify the fats; or a mixture of about equal quantities of oils and resins (preferably colophony) or of resins alone (preferably in half the molecular proportion of the phenols) may be used instead of the oil or fat.—C. A. M.

*Cellulose esters; Varnishes with a basis of*—. L. Clément and C. Rivière. Fr. Pat. 479,387, July 26, 1915.

ETHYL acetoacetate and methyl acetoacetate are employed as the least volatile constituents of solvents for cellulose esters, particularly cellulose acetate, to prevent deposition of moisture and precipitation of the ester during the drying of the varnish. For example, a varnish composed of cellulose acetate, 10 grms., acetone 40 grms., alcohol 25 grms., benzene 25 grms., and ethyl acetoacetate 10 grms., dries in air to a bright transparent film.—F. S.

*Coumarone resin; Manufacture of hard, pale-coloured*—. F. H. Meyer, Hannover-Hainholz. Ger. Pat. 294,107, Feb. 1, 1916.

SOLVENT naphtha is polymerised in the usual manner by treatment with acid (compare Ellis and Rabinovitz, this J., 1916, 1025) and then vigorously agitated with a slight excess of powdered alkali or alkaline-earth carbonates, preferably with addition of a small quantity of sodium or barium peroxide, until the acid is completely neutralised. The liquid is separated by decantation, filtration, or centrifuging, and volatile constituents removed by distillation.—A. S.

*Sizing of wooden articles; Waterproof*—. H. Grünewald, Hanover. Ger. Pat. 293,365, Nov. 8, 1914.

AFTER applying the size, the articles are immersed in a bath of formaldehyde for at least 12 hours and then dried.—A. S.

#### XIV.—INDIA-RUBBER; GUTTA-PERCHA.

*Rubber latex; Treatment of*— with sodium formaldehyde hydrosulphite. A. Dubosc, Caout. et Gutta-percha, 1916, 13, 9031—9032.

It is doubtful whether the small quantity of sodium bisulphite used in order to produce pale rubber from *Hevea* latex is sufficient to destroy the colour-producing enzymes, as suggested by Beadle and Stevens (this J., 1915, 1104), but there can be no doubt that the small quantity of colouring matter already formed is bleached by the sulphur dioxide liberated in presence of acetic acid. Strongly coloured crêpes can be decolorised by the action of hot or cold solutions of sodium formaldehydesulphoxylate, especially in presence of a small quantity of bisulphite, and the use of the former substance and its congeners (known commercially as *Rongalites* or *Hyraldites*) in preference to bisulphite is suggested. The action of these substances is at once reducing, as hydrosulphites, and antiseptic, as aldehyde derivatives.—E. W. L.

*Hevea latex; Distribution of nitrogen in coagulum and serum of*— on coagulation with acetic acid. B. J. Eaton and F. W. F. Day. Agric. Bull. Fed. Malay States, 1916, 4, 350—353.

LATEX was diluted with water until it contained 1.5 lb. dry rubber per gallon. One gallon of

diluted latex was coagulated with 3 oz. of a 5% solution of acetic acid, and the coagulum was left in the serum overnight. 100 parts by weight of latex (containing 0.11% N) yielded 67 parts of wet coagulum, containing 0.15% N and 33 parts of serum containing 0.06% N. In 60 days the nitrogen content of the serum fell to 0.03%, whilst in 6 weeks that of the coagulum fell from 0.78 to 0.23%, calculated on dried coagulum. The greater part of this must have disappeared in gaseous form. Sheet and crêpe prepared on the day following coagulation contained respectively 0.38 and 0.40% nitrogen. In the partially dried coagulum the nitrogen is distributed uniformly through the mass, except in the skin, where, owing to drying of the coagulum and exuded serum, the proportion was found to be about three times as great (0.32%) as in other parts of the slab (0.10–0.12%). The rough scales of dried serum were removed from the surface before analysis.—E.W.L.

"Coagulatex": a new coagulant. B. J. Eaton. Agric. Bull. Fed. Malay States, 1916, 4, 355–356.

"COAGULATEX," advertised as a substitute for acetic acid, is a heavy yellow liquid of sp.gr. 1.4075 at 15°C. It consists essentially of sulphuric acid, of which it contains 50%. 2–3% of ordinary concentrated hydrochloric acid was also present in the sample examined, together with 2.3% of a white crystalline residue, probably consisting of acid sulphates. The value of this product as a coagulant depends entirely on the sulphuric acid present, and it is therefore not a desirable coagulant. Its price also compares unfavourably with that of sulphuric acid.—E.W.L.

#### PATENTS.

Rubber and rubber-like materials; Process of treating —. W. J. Mellersh-Jackson, London. From Rubber Regenerating Co., New York. Eng. Pat. 12,943, Sept. 9, 1915.

SEE U.S. Pat. 1,158,843 of 1915; this J., 1915, 1261.

Plastic and like materials [e.g., rubber]; Roller apparatus for masticating — and for other purposes. J. H. Nuttall, Manchester. U.S. Pat. 1,200,226, Oct. 3, 1916. Date of appl., Feb. 19, 1915.

SEE Eng. Pat. 22,105 of 1914; this J., 1916, 371.

Elastic material for use in tyres and other objects; Process for the manufacture of —. M. Barri-cell, Bygdö, Norway. U.S. Pat. 1,200,290, Oct. 3, 1916. Date of appl., July 18, 1914.

SEE Eng. Pat. 17,242 of 1914; this J., 1916, 266.

### XV.—LEATHER; BONE; HORN; GLUE.

Tanning and wattle bark extract industries in South Africa. Board of Trade J., Nov. 2, 1916.

THERE are at present about twenty tanneries in the Union of South Africa, mostly in Cape Province. The output of leather from these tanneries is now valued at over £500,000 annually; in 1914 the value was £260,000. A certain amount of leather is exported, and during this year about £3500 worth has been sold in the United Kingdom. The manufacture of wattle bark extract from bark grown in Natal has now commenced; one firm is treating 50 tons of green bark daily and a second company expects to commence work within a few months. The first consignment of extract has already been sent to the United

Kingdom. Exports of wattle bark in 1915 amounted to 40,027 tons, a decrease of about 18,000 tons compared with 1914; the decrease is attributed to difficulties as to cargo space.

Utilisation of the tar from gas producers using lignite as fuel. Fischer and Schneider. See III.

#### PATENTS.

Hides and skins; Conversion of — into leather. A. T. Hough. London. Eng. Pat. 17,137, Dec. 6, 1915.

AFTER the usual preliminary treatment, the hides are tanned by steeping them in a solution of an alkali silicate or a solution containing colloidal aluminium silicate, soluble or colloidal silicic acid, or other silicon derivative, with or without the addition of sodium chloride. The process may be used in conjunction with other methods of tanning. (Reference is directed, in pursuance of Sect. 8, Sub-sect. 2, of the Patents and Designs Act, 1907, to Eng. Pat. 100,163; this J., 1916, 854.)—C. A. M.

Salicylic acid or its homologues and formaldehyde; Manufacture of condensation products [tanning agents] from —. Deutsch-Koloniale Gerb- und Farbstoff-Ges., Karlsruhe. Ger. Pat. 293,868, May 16, 1913.

ONE part by weight of salicylic or cresotic acid is condensed with formaldehyde in presence of not more than 2–1 parts of concentrated sulphuric acid, the mixture being cooled to prevent sulphonation. The products are free from sulphur and are valuable tanning agents.—A. S.

Leather substitutes; Production of —. E. Meszaros, Budapest. Ger. Pat. 293,751, June 16, 1914. Under Int. Conv., Jan. 24, 1914.

ANIMAL textile fibres are treated first in dilute sulphuric acid or the like, heated nearly to boiling, and then in a mixture of glue, rosin, Venetian turpentine, and galeum, the specific gravity of which is the same as that of the fibres and which is also heated nearly to boiling. The product remains plastic for a time but subsequently sets and becomes waterproof.—A. S.

Leather and products resembling leather; Manufacture of —. W. Speltzholz, Leipzig, and K. Haring, Assignor to Anhydrot-Leder-Weirke A.-G., Hersfeld, Germany. U.S. Pat. 1,200,146, Oct. 3, 1916. Date of appl., Dec. 13, 1912.

SEE Ger. Pat. 273,652 of 1911; this J., 1914, 759.

Glue and the like; Process of making —. W. M. Grosvenor, Ridgewood, N.J., Assignor to Perkins Glue Co. U.S. Pat. 1,200,488, Oct. 10, 1916. Date of appl., Nov. 25, 1912.

SEE Addition of Jan. 11, 1913, to Fr. Pat. 436,297 of 1911; this J., 1913, 761.

Condensation products [from phenols and formaldehyde] and method of manufacturing a substance capable of replacing ivory, mother of pearl, celluloid, etc. Fr. Pat. 478,881. See XIII.

### XVI.—SOILS; FERTILISERS.

Chalking: a useful improvement for clays overlying the chalk. E. J. Russell. J. Board Agric., 1916, 23, 625–632.

THE old practice of sinking chalk pits and spreading the chalk over the surface of clay land has not

been common of recent years owing to the fact that stable manure, artificial fertilisers, and ground lime have been more readily obtainable, but experience has shown that better results are obtained with chalk. The essential feature of the method is that the chalk is dug out from the field to which it is to be applied. From 50 to 60 loads (a load is about 20 bushels) of chalk is spread over each acre and the dressing usually lasts for 25–40 years; the annual loss is about 1.5 load per acre. The chalk dressing renders clayey soil more porous and draining is facilitated, the soil is easier to plough and work down to a fine tilth, and yields better crops of clover and barley. Swedes and turnips are less liable to "finger-and-toe" disease when grown on chalked land, but winter oats and potatoes do not give any extra return.—W. P. S.

*Silica; Quantitative determination of the — in soils.* B. von Horváth. Z. anal. Chem., 1916, 55, 513–536.

THE estimation of the amorphous silica set free when a soil is extracted with hydrochloric acid is usually performed by digesting the insoluble residue from that extraction with alkali hydroxide or carbonate solution, treating the filtered solution with hydrochloric acid, evaporating to dryness, and weighing the separated silica. Theoretical considerations having cast doubts upon the validity of this general method, six well-known modifications of it were submitted to a thorough investigation. The selected soil was digested with hydrochloric acid (sp.gr. 1.115) at a raised temperature for 5 days, filtered off, washed, and dried at 100° C.; 5-grm. portions were then taken and treated in silver dishes on the water-bath with 100 c.c. of the selected solvents, which consisted of aqueous solutions of sodium and potassium hydroxides and carbonates, and also of diethylamine. The results obtained were very discordant, the extreme variation being 60%. It was found that the amount of silica dissolved depended upon the nature of the dissolved alkali compound, upon its concentration, and on the time of action: upon the temperature during extraction, and on the temperature to which the original soil, or its HCl-extract, had been subjected: upon the size of the soil particles, upon the amount of agitation, and upon the ratio of the amount of soil to the amount of solvent. All the methods investigated had the defect that the alkaline solution dissolved not only the silica liberated by hydrochloric acid, but also that derived from other sources. The greater part of the excess silica found resulted from the action of the solvent solution upon silicates, a small quantity came from quartz particles, and a very small quantity from the original amorphous silica of the soil. The amount of liberated silica found by these methods varied with the conditions under which the soil was treated with acid, i.e., with its concentration and with the time of action. It is possible that the use of weaker bases, e.g., certain organic bases, would give more reliable results.—E. H. T.

*Phosphorus compounds of the soil; Reaction between dilute acids and the —.* E. J. Russell and J. A. Prescott. J. Agric. Sci., 1916, 8, 65–110.

DETERMINATIONS of the amounts of phosphoric acid removed from soils by the action of dilute acids afforded new evidence that the soil cannot be regarded merely as a collection of inert matter containing small quantities of soluble constituents. 50 or 100 grm. portions of five different kinds of soil were digested with 1 litre of dilute acid at 23° C. for a definite time, and the dissolved phosphorus compounds were then determined. In

every case the amount so extracted was found to increase continuously with the concentration of the acid, the increases being nearly proportional to the concentration. All the dilute acids used, when of equal concentration, gave extraction curves of the same type, but the amount of action was less with the strong acids than with citric or oxalic acids, and it was not proportional to the time. Using acids of  $N/20$ – $N/10$  concentration, it was found that the amount of phosphorus compounds extracted diminished with the time, so that less was dissolved out in 24 hours than in 10 minutes. Hence a reverse action, slower than the direct action, must take place. As experiments proved that the reverse action was not due to precipitation, it was inferred that the cause was to be found in the soil itself. When disodium phosphate was added to the mixed soil and acid, some of it was absorbed by the soil, and this absorption occurred even when the concentration of acid was  $N/5$ , though to a less extent than when  $N/10$  acid was present. The absorption of the  $P_2O_5$  ion is of the same kind as adsorption by colloids. It varies considerably with the nature of the acid, being greatest for hydrochloric and nitric acids, and least for citric acid of equivalent strengths. The greater power of citric acid to extract phosphorus compounds from the soil is due, not to its greater solvent action, but to the fact that in its presence the reverse action of adsorption is least. When, by means of a diffusion process, the reverse actions were prevented, it was found that the quantity extracted was the same for hydrochloric, nitric, and citric acids, and somewhat greater for sulphuric acid. Determinations of "available  $P_2O_5$ " do not give the true quantities of phosphorus compounds dissolved, and the results vary with the nature of the acid used and with the experimental conditions. Comparative determinations upon soils of the same type would, however, be useful, but only when the soil has been surveyed and definite types have been established. The order in which the acids themselves are adsorbed by soil is: oxalic and citric (most), phosphoric, sulphuric, hydrochloric, and nitric. Little phosphoric acid is adsorbed by the soil in presence of citric or oxalic acid, probably because its adsorptive capacity is satisfied by the latter acids. The amount of adsorption of phosphoric acid by the soil depends also upon the time; with nitric acid the amount increases, but with citric acid it is less after 24 hours than after 1 hour. The adsorption is probably instantaneous, and is influenced by chemical changes effected by the acid in which silica is liberated; but the adsorptive capacity does not appear to be affected by the presence of the acid as such.—E. H. T.

*Absorption; The phenomenon of — in its relation to soils.* J. A. Prescott. J. Agric. Sci., 1916, 8, 111–130.

THE removal of salts and colouring matters from solution by the action of sand or soil has been known since very early times (Aristotle); but the first definite agricultural observation was made by Gazzeri in 1819, when he recorded that soil, especially clay soil, takes up soluble substances which might afterwards become available for plant nutrition. Lambroschini (1830) suggested that a loose kind of combination took place between the soil and the nutrient matter absorbed by it, and H. S. Thompson (1845) investigated quantitatively the effect of adding ammonium sulphate to soil and then extracting with water. He found that much of the ammonia remained in the soil and that it was replaced in solution by calcium and magnesium, a phenomenon that is now called "base-exchange." These observations were extended by J. T. Way (in 1850), who gave them a

chemical explanation in opposition to Matteucci, who thought the action was purely physical. According to Way, the action is due to the precipitation of insoluble substances, e.g., double silicates of calcium and magnesium react with the added ammonium or potassium salt yielding insoluble alkali aluminium silicates and setting free calcium and magnesium salts. A. Voelcker and Warington supported the chemical hypothesis and Liebig accepted the physical explanation, regarding the nutritive capacity of a soil as depending solely on the quantity of nutrient substances physically retained by it. Since 1880 very few new facts have been discovered, the main development having been on the theoretical side. Two practical methods have been in vogue: the soil is either brought into equilibrium with a definite volume of solution, or the latter is filtered through a column of soil; the former method is the more accurate. Valuable work was done by Knop and Biedermann (1871), by Kellner (1880), and recently by Ramann, in establishing the law that the amounts of bases removed by soils are equal to the quantities taken up by the vegetation growing in them. Although small temperature changes are without appreciable effect on soil absorption, W. Schuhmacher (1897) found that it was usually less at high temperatures than at low. The part played by humus has received little attention. The author has shown that the amount of phosphoric acid absorbed by humus is independent of the concentration of the phosphate solution employed. The connection between soil problems and colloidal phenomena was first indicated by Van Bemmelen (1883). Convinced by the fact of "base-exchange," he at first favoured Way's interpretation, holding the silica "gel" in the soil to be the main factor in soil absorption; but later work on simple gels, e.g., silica, iron oxide, and alumina, and neutral solutions, where the possibility of chemical action was extremely remote, led him to the conclusion that soil absorptions are of the same kind as ordinary physical absorptions. Recent work has confirmed this view; soil absorption is of the same nature as physical adsorption—"the concentration of any substance on the surface of another"—increasing with the concentration of the solution according to a simple mathematical relationship. The absorption of dyestuffs by the soil proceeds in accordance with the laws of adsorption. The phenomena of "base-exchange" have been shown to be governed by the same laws by Patten, Cameron, Parker, and Wiegner. The last-named has shown that the removal of ammonia by "permutite" from ammonium chloride solution follows the adsorption laws very closely; the equilibrium is instantaneous, the chlorine ion is not absorbed, and the absorption diminishes with rise of temperature. The reaction between the soil and phosphates in presence of a dilute acid obeys the adsorption equilibrium law (see previous abstract), and percolation experiments with soil containing monocalcium phosphate gave results in agreement with the assumption that the concentration of the percolate at any moment is proportional to the amount of absorbed substance.

—E. H. T.

*Ammoniacal nitrogen of peats and humus soils.*  
J. C. B. Ellis and C. G. T. Morison. *J. Agric. Sci.*, 1916, 8, 1—8.

The determination of the ammonia liberated from soils by distillation with magnesia, was conducted in a litre flask fitted with a trap and a tube conveying a current of ammonia-free air. To the trap was connected a 100 c.c. pipette, which passed through the cork of a filter flask. The latter contained 100 c.c. of N/100 acid, and its side tube communicated with a filter pump.

In this way the distillation was effected under greatly reduced pressure at about 40° C. The excess acid was titrated in presence of methyl orange. Experimenting with 30 grm. portions of three kinds of air-dried peat and using 3 grms. of magnesia, it was found that the greater part of the ammonia passed over during the first two hours, and it was inferred that 3 hours would suffice to expel the whole of the nitrogen derived from the more unstable nitrogen compounds. Distillations with eight different peat soils and three arable soils showed that the former evolved much more ammonia than the latter, and acid peats gave more than neutral peats. When the aqueous extracts of air-dried peats were distilled with magnesia, it was found that 50—80% of the ammonia, as obtained above, was recovered. The amounts of ammonia that were set free by distillation and that were removed in the aqueous extracts, showed marked variations with the depths from which the soil samples were taken.

—E. H. T.

*Ammonification by certain soil fungi; Effect of soil reaction on —.* N. Kopeloff. *Soil Sci.*, 1916, 1, 541—573. *J. Chem. Soc.*, 1916, 110, i, 702—703.

*Rhizopus nigricans*, *Zygorrhynchus Vuilleminii*, and *Penicillium* are equally affected by changes in the reaction of the soil; such changes have a greater effect when dried blood is employed as source of nitrogen than with cottonseed meal, and in clay soils as compared with sandy soils. The maximum accumulation of ammonia by these fungi occurs between the neutral point and an acidity equivalent to 2000 lb. of calcium oxide per acre. Acidity greater than this, and an increase in alkalinity beyond the neutral point, generally cause a depression in ammonia production. It is suggested that ammonification by fungi may be of practical importance under conditions unfavourable to soil bacteria.

*Protein decomposition in soils.* E. C. Lathrop. *Soil Sci.*, 1916, 1, 509—532. *J. Chem. Soc.*, 1916, 110, i, 703.

A SANDY loam soil was thoroughly mixed with dried blood (40 : 4) and kept for two hundred and forty days in a jar covered with perforated paper. The percentage of water in the soil was kept at 10%, water being added at intervals of five to eight days, when the soil was turned out and mixed to promote aeration. Samples were taken for estimating the different forms of nitrogen after eighteen, forty-four, eighty-six, one hundred and forty-eight, and two hundred and forty days. Ammonification was very rapid during the first eighty-six days, after which there was a marked fall until the end of the experiment, when the production of ammonia was only at about 10% of the rate observed after the first eighteen days. In two hundred and forty days 79% of the blood protein was converted into ammonia. Of the nitrogen of the monoamino-acids about 89% was converted into ammonia, whilst arginine and histidine each gave about 83%. Indications were obtained that new protein substances were formed, and that these are more resistant to the action of micro-organisms than the proteins of dried blood. The lysine of the dried blood disappeared almost completely in eighty-six days, whilst during the last one hundred and fifty-four days there was a continual increase in this form of nitrogen. At the end of two hundred and forty days the soil contained protein-like substances soluble in 1% sodium hydroxide. It is uncertain whether these substances form undecomposed residues of the dried blood, or whether they are newly formed proteins.

*Manganese soils; Effect of some — on ammonification and nitrification.* P. E. Brown and G. A. Minges. *Soil Sci.*, 1916, 2, 67—85. *J. Chem. Soc.*, 1916, 110, 1, 703—704.

The soil employed was a clay loam, containing 0.1732% of manganese. In the ammonification experiments the soil received 5% of dried blood, whilst for nitrification 0.1 grm. of ammonium sulphate was added. Manganese chloride, applied at the rate of more than 2000 lb. per acre, retarded both ammonification and nitrification. Applications of 100 and 200 lb. increased ammonification slightly and nitrification distinctly. Manganese sulphate increased both ammonification and nitrification when applied at the rate of 100 lb. per acre, whilst large amounts (2000 lb.) had a depressing effect. Manganese oxide applied at the rate of 2000 lb., or more, per acre retarded both ammonification and nitrification.

*Lead; Action of — as a stimulant for plants.* A. Stutzer. *J. Landw.*, 1916, 64, 1—8. *J. Chem. Soc.*, 1916, 110, 1, 704.

The results of water culture experiments with rye, wheat, oats, barley, maize, and peas showed better growth when a portion of the nitrogen was in the form of lead nitrate than with sodium nitrate only. The best plants, especially barley, were obtained in solutions containing 0.5 grm. of lead nitrate per litre. In field experiments the yields of sugar beet and of sugar were considerably increased by application of 4 kilos. of lead nitrate per hectare. With oats the yield of grain was increased, whilst the yield of straw was diminished. The same amount of lead nitrate (4 kilos. per hectare) gave unsatisfactory results with potatoes, which seem to be very sensitive to lead nitrate. Another field experiment, with wheat, showed that whilst lead nitrate gave good results in conjunction with 50 kilos. of nitrogen as sodium nitrate, the results were much less satisfactory when smaller amounts of sodium nitrate were employed.

*Soils; Comparison of the nitrifying powers of some humid and some arid —.* C. B. Lipman, P. S. Burgess, and M. A. Klein. *J. Agric. Res.*, 1916, 7, 47—82.

The nitrifying powers of about 45 humid, and of about 150 arid soils were determined under laboratory conditions. The humid soils included a typical soil from every State or Territory in the United States, and the arid soils represented the different types of four soil-survey areas in California. The nitrifying power of each soil was determined on the soil nitrogen itself, and on the same with the addition of 0.2% ammonium sulphate, 1% dried blood, or 1% cottonseed meal, the nitrate being estimated by the phenoldisulphonic acid method. The 100-grm. soil portions, containing the optimum amount of moisture, were incubated for one month at 28°—30° C. As a class, the humid soils contained more total nitrogen than the arid soils, but no relationship between this content and the power of nitrification could be traced. In the humid soils, nitrification was greatest in presence of dried blood and least in presence of ammonium sulphate; in fact, the amount of nitrate produced from soil nitrogen was less when the ammonium salt was present than when it was absent. The nitrifying powers of arid soils were generally less than those of the humid soils; the power was increased by ammonium sulphate and by cottonseed meal but decreased by dried blood. This retarding action of 1% of dried blood in an arid soil may be due to the circumstances that ammonia is rapidly produced from this fertiliser in the ammonification stage, that ammonia is fatal to the nitrifying organisms, and that it is less readily adsorbed

and eliminated in such soils than in moist soils rich in humus and organic colloids. Less nitrate was produced from the soil with added ammonium sulphate than from the soil alone in 88% of the humid soils, but only in 19% of the arid soils; with dried blood the percentages were 20 and 48 respectively, and with cottonseed meal 46 and 24, but the extent of nitrification in arid soils containing the last-named fertiliser varied very considerably. Thus different forms of fertiliser nitrogen produced widely different results on different soil types.—E. H. T.

*Phosphates contained in mineral phosphates; The nature of the —.* G. S. Robertson. *J. Agric. Sci.*, 1916, 8, 16—25.

PHOSPHATIC rocks from seven different sources were analysed, and the  $P_2O_5$  and lime contents of the citric-soluble portions also determined. In the case of the harder rocks, the ground material was separated by means of sieves into five different grades of fineness and each grade was analysed separately. The citric solubility was found by subjecting 5-grm. portions to consecutive extractions with 2% citric acid solution, and test experiments with apatite showed that the lime and phosphoric acid were dissolved out in the same ratio as they were present in the mineral. The analyses of the citric-soluble fractions indicated the presence of the following compounds: Makatea Island phosphate,  $2Ca_3P_2O_7 \cdot CaO$ ; Florida pebble and Tunisian,  $4Ca_3P_2O_7 \cdot CaO$ ; Algerian, Gafsa, and Belgian,  $Ca_3P_2O_7 \cdot CaO$ ; apatite,  $3Ca_3P_2O_7 \cdot CaO$ . The results with apatite indicate that the ratio  $P_2O_5 : CaO$  is not different if the oxygen of one of the  $CaO$  groups is replaced by fluorine or chlorine, a fact which would account for the lower solubility of rock phosphate in citric acid as compared with bone meal; and the higher lime content would explain the higher solubility in citric acid as compared with apatite (see Robertson, this J., 1916, 216—217). In general, the solubility increased with the amount of lime combined with phosphoric acid, thus confirming the observations made by Collins on basic slag (this J., 1915, 527). The effect of calcining the rock phosphates in a muffle furnace was to diminish greatly the citric solubility. Calcination causes the production of a "silica phosphate" which is soluble in the first citric solution, and also of one or more phosphates with a lower (combined) lime content than the mineral. The longer the calcination the greater the change in this direction. (Compare Aita, this J., 1916, 1074.)—E. H. T.

*Oxygen derived from the reduction of nitrates by green plants; Liberation of —.* M. Molliard. *Comptes rend.*, 1916, 163, 371—373.

COMPARATIVE experiments in which radishes were grown in a confined volume of air and in similar culture media (except that nitrogen was supplied in some cases as potassium nitrate and in others as ammonium chloride) showed that the fixation of nitrogen from a nitrate was accompanied by a characteristic liberation of oxygen. The pressure developed accorded with an evolution of 2 atoms of oxygen for each atom of nitrogen fixed.

—F. SODN.

*Loss of phosphoric acid during fusion with ammonium fluoride.* Davis and Prescott. See XXIII.

#### PATENTS.

*Peat; Treatment of —, and production of a preparation suitable for use in horticulture and agriculture.* J. J. A. and H. C. S. de Whitley, Lee, Kent. *Eng. Pat.* 14,487, Oct. 13, and 17,848, Dec. 21, 1915.

BLACK or dark peat is treated with just sufficient

ammonia to render it slightly alkaline, and then 5–20% of its weight of calcium carbonate, or similar substance, is added to prevent subsequent development of acidity. The ammonia may be generated within the peat mass by the action of an alkali, alkali carbonate, or alkaline earth upon an ammonium salt, both ingredients being added directly to the peat and well stirred in. Thus, for example, one ton of partly dried peat, containing about 35% of moisture, may be mixed with 2 cwt. of ammonium sulphate, either solid or dissolved, and 2 cwt. of powdered potassium carbonate, and subsequently with 1–4 cwt. of calcium carbonate. The fertilising value may be enhanced by the addition of potassium compounds, phosphates, etc.—R. H. T.

*Sterilisation of soil; Process and apparatus for the* — F. Minervini. Fr. Pat. 479,056, June 17, 1915.

STEAM is introduced into the soil at a temperature, under 4 pressure, and in quantity sufficient to raise the mass of earth to about 120° C., the temperature being maintained for a sufficient length of time to sterilise the soil. The plough is provided with one or more steam boilers, connected by a distributor tube to a number of injectors, consisting of a series of tubes pierced with holes, the openings being covered by bells. During the treatment, the soil and the injectors sunk in the soil are covered by impermeable cloth bands, preferably mounted on wood frames. When applied to arable land, the plough is provided with an arrangement for sinking the injectors at the side, between the plough-share and the draught animals, in the preceding furrow, the injectors being immediately covered automatically by the earth thrown up by the plough in forming the furrow.—B. N.

*Electrolytic manufacture of caustic potash.* Fr. Pat. 478,371. See VII.

*Preparation of tetracupric sulphate and its use as a fungicide.* Addition to Fr. Pat. 476,512. See XIX.

## XVII.—SUGARS; STARCHES; GUMS.

*Reducing sugars; Supposed precipitation of — by basic lead acetate. Estimation of carbohydrates.* V. W. A. Davis. J. Agric. Sci., 1916, 8, 7–16.

IN opposition to the general belief that levulose is precipitated from solution by basic lead acetate, it is shown that no such action occurs in dilute solution, even in the presence of such salts as chlorides, sulphates, or carbonates. There is however a loss of this sugar if the lead salt be kept in the liquid for a considerable time. Thus, 100% of levulose is recoverable if the lead is precipitated immediately after addition of the acetate, but if it is left in solution for 15 mins., 1 hour, or 24 hours, and then eliminated, increasing amounts of sugar disappear, and at the same time the liquid becomes more and more yellow. The loss of levulose ranged from 20% to 30%, but the values found by reduction were always 13–14% higher than those calculated from the rotatory power. The discrepancy is due to the conversion of levulose into glucose,  $C_6H_{12}O_6$ , a substance which has a lower reducing power than levulose, and is optically nearly inactive. The conversion is accelerated when the temperature is raised. The use of normal lead acetate to clarify liquors containing reducing sugars is not recommended.

Experience has shown that the sugars in leaf material can be determined accurately if the basic acetate be added, little by little, until precipitation is complete, excess being carefully avoided. Usually 5 c.c. of acetate solution to 500–500 c.c. of liquid is sufficient. The precipitate should be filtered off immediately, and then washed thoroughly; the excess of lead salt is removed with sodium chloride or sulphate. By observing similar precautions, tannin admixed with sucrose and reducing sugars can be precipitated without loss of sugars. Dextrose and maltose are not affected by hot digestion with basic lead acetate.—E. H. T.

*Molasses; Colouring matter of —.* H. Stoltzenberg. Ber., 1916, 49, 2021–2023.

BET sugar molasses and the residue from the desaccharification process, after extraction with alcohol, still contain a brown non-fluorescent colouring matter, which can be extracted by precipitating with lead acetate, decomposing the precipitate with hydrogen sulphide, evaporating the filtrate in a vacuum, and diluting the resulting syrup with water. On standing it slowly precipitates as a black amorphous substance, very slightly soluble in water, and still less so in organic hydroxy compounds, insoluble in chloroform, ethyl acetate, etc. It decomposes at 100° C., forming a black resin. Its composition corresponds to the formula  $C_{12}H_{11}N_2O_2$ . Its solubility in alkali points to the presence of hydroxyl groups, whilst basic nitrogen is indicated by its solubility in acids. It is unsaturated and on reduction in alkaline medium gives a grey substance insoluble in alkali, and a yellowish solution in acid medium. The yield of colouring matter amounted to 1.2 grms. from 1 kilo. of molasses.—G. F. M.

*Wheat-starch industry; New methods in the —.* C. Goldbeck. Chem.-Zeit., 1916, 40, 829–830.

MODERN methods of starch manufacture enable a larger yield to be obtained from the flour than was possible with the older methods, this being attained by a more perfect separation of the starch from the gluten. The following method gives a yield of 58–60% of starch as compared with 34–52% by the old methods. The flour is kneaded into a dough with water and washed in an extractor; the starch-milk obtained is passed through the usual sieves and the fine starch then separated by centrifugal action. The portion of the starch still remaining mixed with the gluten on the sieves is separated by subjecting the gluten to fermentation or treatment with dilute ammonia and acetic acid, and centrifuging the mixture. The gluten and a small quantity of bran separated in the process may be used as feeding stuffs.—W. P. S.

*Formation of methylglyoxal and formaldehyde in glycolysis.* Sjölema and Kam. See XVIII.

*Influence of strong salt solutions on the spontaneous oxidation of pyrogallol, ferrous sulphate, and levulose.* MacArthur. See XXIV.

### PATENTS.

*Sugar refining.* R. A. Chesebrough. Fr. Pat. 479,506, Aug. 13, 1915.

A FILTERING and decolorising agent is employed, made by impregnating dried, ground, and sifted fullers' earth with petroleum, of sp.gr. preferably below 34° B. (sp. gr. 0.854), and heating in an oven or retort at red heat. A layer of carbon is thus deposited on the particles, rendering them insoluble in water, so that the pores of the filter do not



become clogged. The prepared material is heated to about 135° F. (57.2° C.) before being placed in the filter, and filtration is conducted at about 130° F. (54.4° C.).—J. H. L.

*Glucose, maltose, starch-syrups, and dextrins; Manufacture of*—Soc. d'Exploit. des Proc. H. Boulard. Fr. Pat. 477,927, July 8, 1914.

SACCHARIFICATION of starch is effected by means of *Mucor Boulard* No. 5 (see Fr. Pat. 464,601; this J., 1914, 497) or similar robust organism. To prepare products containing a high proportion of dextrose, and very little maltose and dextrins, the amylaceous material may be heated for 35 mins. under 3½ kilos. pressure with some water and 0.5–0.8% of acid, then transferred to a closed vat provided with means for aerating, and seeded at 40° C. with a small quantity of the mould. When saccharification is complete, the filtered liquid, which does not require neutralisation, can be concentrated; it yields quite colourless syrups without treatment with charcoal. Products containing a high proportion of dextrins may be prepared by employing certain acids for the preliminary digestion, and aerating more strongly during saccharification.—J. H. L.

*Sugar and like rolling mills.* J. Miller, and G. Fletcher and Co., Ltd., Derby. Eng. Pat. 101,693, Aug. 5, 1916. (Appl. No. 11,075 of 1916.)

*Process of producing oxalic acid from sugar and other carbohydrates.* Eng. Pat. 101,680. See VII.

## XVIII.—FERMENTATION INDUSTRIES.

[Breuing.] *Pre-mashing, proteolytic digestion, and protein turbidity.* W. Windisch. Woch. Brau., 1916, 33, 105–108, 121–125.

PRE-MASHING, i.e., the digestion of malt in cold water before the mashing process, has a favourable influence on transformations in the mash, by rendering the material more easily attacked by the malt enzymes and by increasing the amount of these enzymes which pass into solution in the wort. The yield of extract is increased, and the chance of starch escaping saccharification and afterwards producing starch-haze is reduced. The possibility of undesirable flavouring and colouring matters of the husk passing into the wort as a result of pre-mashing, may be avoided by first screening the grist and adding the husk fraction only after pre-mashing is completed; this is specially recommended when waters rich in carbonates are used. Pre-mashing should invariably be conducted at a low temperature, to prevent the development of excessive acidity; at 5°–10° C. the process may be continued safely for 6, 9, or even 12 hours, provided that the mashing process proper is commenced as soon as the temperature is allowed to rise. The author discusses the practice of proteolytic digestion, i.e., the holding of mashers for a time at 50° C. to promote proteolysis (see this J., 1912, 654), and gives examples of its application to the decoction method of mashing. Its chief benefit is that it tends to free the wort from proteins likely to separate later in the form of a haze or turbidity in the beer, and it is therefore of most service with malts of deficient modification, such as the short-grown malts widely used in Germany at present. Pre-mashing and proteolytic digestion have been wrongly held responsible for sluggish fermentations, but they are rather a remedy than

a cause. Such fermentations are most common when highly nitrogenous and poorly modified malts are used, the worts from which are liable to contain abnormally large amounts of imperfectly dissolved colloidal protein matters. The deposition of these colloids on the yeast cells is the cause of slow and arrested fermentation. Their elimination by decomposition into simpler and more soluble substances, before fermentation, can in many cases, if not in all, be brought about by pre-mashing and proteolytic digestion. A high wort acidity, produced for example by the use of *Bac. Delbrücki* (see this J., 1913, 955), also assists in the elimination of undesirable proteins from the wort, by promoting their separation in a flocculent form on the wort cooler.—J. H. L.

*Fermentation; Acceleration of*—by certain materials. H. Wüstenfeld. Woch. Brau., 1916, 33, 89–90.

THE author criticises the explanation suggested by Moufang for the observed accelerating effect of dead yeast on fermentation (see this J., 1913, 303; 1915, 1159). The cell walls of dead yeast lose their property of selective permeability, and in Moufang's experiments enzymes from the surrounding liquid may have entered the cells and produced substances having a stimulating action on the living yeast. A more probable explanation is, however, that the dead cells and other materials prevented, in a purely mechanical manner, supersaturation of the liquid with carbon dioxide, which has a somewhat toxic influence on yeast, and that in consequence of the freer evolution of gas from the liquid the latter was kept in more rapid circulation. The presence of grains in distillers' worts accelerates fermentation in a similar manner.—J. H. L.

*Beer; Sensitiveness of*—towards cold, and the Wallerstein process. P. Petit. Brasserie et Malterie, 1916, 6, 161–166.

DETAILS are given of trials made by a number of French brewers with Wallerstein's peptonising agent for rendering beers chill-proof (see U.S. Pats. 995,824 and 997,873; this J., 1911, 916, 1027). The substance, a white powder, was added after the primary fermentation, at the rate of ¼ oz. per barrel of beer. Provided it was allowed to act for a sufficient time it gave very satisfactory results, rendering the elimination of gluten by chilling and filtration unnecessary, and having no undesirable effects on other characters of the beers, such as retention of head. The time required was found to depend on the temperature, viz., 3 days at 15° C., 12–15 days at 10° C., or 30–40 days at 2°–3° C. The addition of finings arrests the action of the substance, and in cases of top-fermentation, where owing to this cause the duration of treatment was insufficient, the beers formed a "glutin-haze" at low temperatures but on warming the haze vanished more readily and completely than in the case of untreated beers.—J. H. L.

*Brewers' filler pulp.* W. A. J. Foster. J. Inst. Brew., 1916, 22, 413–424.

PULP equal in quality to the German products, which were exclusively used before the war, is now made in this country. The raw materials which have been used for the manufacture of brewers' pulp are cotton, linen, jute, wood, and wool fibres, and sometimes small quantities of asbestos, but cotton usually forms the main constituent and the best pulp is made from this alone. A pulp possessing a good white colour and guaranteed unbleached, can only have been made from clean cotton fibre. The moisture-content of such a pulp

should not exceed 10%, or mouldiness may develop. The ash-content should be less than 1% unless asbestos has been added. The author does not recommend the addition of asbestos, but brewers desiring it should add it themselves. The pulp should contain no substances soluble in hot or cold water or alcohol, and should impart no flavour to these liquids. A cake of pulp should disintegrate readily in boiling water, and give rise to a flaky and homogeneous mass free from knots or balls. The author describes the microscopic appearance of cotton, linen, jute, wood, and wool fibres and some tests to distinguish them. The commonest defect in pulp is the formation of knots or balls. This may be due to the use of unsuitable fibres or their improper treatment during manufacture, but it is often produced by wrong methods of handling, especially during washing. Apparatus for washing pulp should not be fitted with paddles or wheels for churning the material. The pulp should be washed with cold water until free from yeast, and then for an hour with water at 168°–190° F. (75°–87° C.), and afterwards again with cold water. Boiling water or live steam should not be used.—J. H. L.

*Brewery; Use of hydrogen peroxide in the*—  
H. B. Wooldridge. *J. Inst. Brew.*, 1916, 22, 436–446.

HYDROGEN peroxide has been successfully applied to the disinfection of casks, filter pulp, and other objects in the brewery. Casks which have become mouldy are steamed for about 15 mins., and then 1 quart, or in bad cases more, of 12-vol. hydrogen peroxide, diluted to 1 gall., is introduced into each; the casks are closed and rolled thoroughly at intervals during several hours. The peroxide penetrates deeply into the wood, destroying moulds and other organisms; it has no injurious action on the wood and leaves no undesirable decomposition products. In the treatment of filter-pulp, this is first washed with cold water and then with water at 160° F. (71° C.); after cooling to about 120° F. (49° C.), 2 quarts of 12-vol. peroxide is added for about 25 lb. of pulp. After standing or half an hour the pulp can be used; it is white and quite sterile. Wooden stoppers are put through in ordinary washing machine and then left for several hours in 12-vol. hydrogen peroxide diluted eight-fold.—J. H. L.

*Vine; Approximate determination of the sugar content of*—  
J. Pritzker. *Schweiz. Verein Anal. Chem.*, May, 1916. *Chem.-Zeit.*, 1916, 40, 832.

THE wine is evaporated to remove alcohol, then treated with lead acetate, filtered, and 2.5 c.c. of the filtrate is placed in a tube similar to that described previously for the determination of sulphates in wine (this J., 1916, 859); boiling Fehling's solution is then introduced into the tube until the latter is filled up to the 10 c.c. mark, the tube is placed in boiling water for 4 mins., then cooled, and centrifuged for 3 mins. Any cuprous oxide adhering to the sides of the tube is now detached with a rubber-tipped glass rod, and, after centrifuging for a further 3 mins., the volume of the cuprous oxide in the capillary portion of the tube is read off; its volume is a measure of the sugar content of the wine. The difference in the amount of sugar found by this method and that obtained by the ordinary gravimetric method varies from  $\pm 0.2$  to 0.3 gm. per litre.—W. P. S.

*Vine; Detection of artificial colouring matters in*—  
H. Kreis. *Schweiz. Verein Anal. Chem.*, May, 1916. *Chem.-Zeit.*, 1916, 40, 832.

DARK red wines, even when diluted with five parts

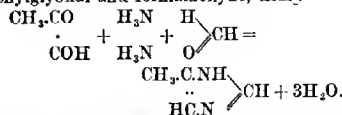
of water, sometimes dye wool so intensely that the colour cannot be removed by washing with boiling water; this may lead to the conclusion that an aniline dye is present in the wine. If, however, the wine is diluted previously with 10 parts of water, the colour is usually removed from the wool when this is washed with boiling water. In doubtful cases the coloured wool should be heated on a water-bath with 1% ammonia; this destroys the natural colouring matter derived from the wine, whilst aniline dyes, for the most part, go into solution. The ammoniacal solution is then acidified with sulphuric acid and heated with a fresh thread of wool. If aniline dyes are present the wool is coloured, but in their absence it remains white.—W. P. S.

*Vinegar and wine; Use of the iodic acid-starch reaction in the control of*—  
J. Jeaprétre, *Schweiz. Verein Anal. Chem.*, May, 1916. *Chem. Zeit.*, 1916, 40, 833.

LANDOLT has pointed out (Ber., 1886, 19, 1317) that a mixture of sulphurous acid, iodic acid, and starch develops a blue coloration after a varying lapse of time. The author shows that if a sulphite and an acid be used instead of free sulphurous acid, the time which the coloration takes to appear depends on the kind and concentration of the acid, the temperature, age of the reagent, etc. For instance, the time elapsing before the blue coloration appears is as follows, when 10 c.c. of the N/10 acid is mixed with 10 c.c. of the reagent (10 c.c. of 0.2% sodium iodate solution, 10 c.c. of 0.2% sodium sulphite solution, and 5 c.c. of 0.5% starch solution, diluted to 100 c.c.):—acetic acid, 438; succinic acid, 320; malic acid, 52; citric acid, 45; tartaric acid, 26 secs.; oxalic acid and mineral acids, at once. Since the presence of a trace of mineral acid greatly reduces the time required for the development of the coloration, the reaction may be used for the detection of mineral acids in vinegar and wine. If 10 c.c. of wine gives a blue coloration in less time than does 10 c.c. of citric acid solution of equal strength, an abnormal quantity of free mineral acid is present. Generally, a non-sulphured, non-plastered wine reacts as slowly as does a succinic acid solution.—W. P. S.

*Glycolysis; Formation of methylglyoxal and formaldehyde in*—  
B. J. Sjollem and A. J. H. Kam. *Rec. Trav. Chim. Pays-Bas*, 1916, 36, 180–193.

IN the breakdown of sugars under biological agencies, e.g., in alcoholic fermentation, and the building up of proteins, the formation of pyruvic acid or its aldehyde, methylglyoxal, in the intermediate stages has been considered very probable. This hypothesis has received support by Windaus and Koop (this J., 1906, 1234) and by Neuberg. The formation of methyliminazole (a histidine derivative) by the action of ammoniacal zinc hydroxide on dextrose was explained by the former authors through the intermediate production of methylglyoxal and formaldehyde, thus:



Although neither methylglyoxal nor formaldehyde can be detected among the products of glycolysis, the hypothesis would be considerably strengthened if it were shown that the synthesis of the nitrogenous complex took place by the condensation of the simpler components by the same reaction more readily than from the more remote dextrose. This has now been done by the authors: 208-5

grms. of an aqueous solution containing 14.9 grms. of methylglyoxal, determined by the semicarbazide method, was mixed with 17.6 grms. of 35% formaldehyde solution and the mixture treated with ammoniacal zinc oxide partly in solution and partly in suspension. A precipitate of the zinc salt of methyliminazole was immediately produced and fully identified with the product obtained by Windaus and Koop from dextrose, which is only formed slowly in the course of some weeks. Neuberg has asserted that dihydroxyacetone in alkaline solution is very readily converted into methylglyoxal and should be capable of the same condensations, but the authors do not confirm this view. Dihydroxyacetone, with or without formaldehyde, only yields the zinc derivative of methyliminazole very slowly, as in the case of dextrose. Further, on treatment with hydrazine it yields a hydrazone which is very different from the product of the action of hydrazine on methylglyoxal, and whereas methylglyoxal condenses very readily with thiourea, dihydroxyacetone does not. The hypothesis founded on the probable formation of dihydroxyacetone as an intermediate product is therefore not supported by the present investigation.—J. F. B.

*Velocity of scission of lactose by action of the Bulgarian ferment.* Quagliariello and Ventura. See XIXA.

*An examination of certain methods for the study of proteolytic action.* Sherman and Neun. See XIXA.

*Comparison of barbituric acid, thiobarbituric acid, and malonylguanidine as quantitative precipitants for furfural [from pentoses].* Dox and Plaisance. See XXIII.

*Reactions of peroxidase purified by ultrafiltration.* Bach. See XXIII.

#### PATENTS.

*Hops; Process for the preparation of an extract of* —. E. W. Kuhn, London. Eng. Pat. 14,330, Oct. 9, 1915.

Hops and cooled wort are introduced into a cylinder such as that described in Eng. Pat. 8823 of 1907 (this J., 1908, 704) until the cylinder is full. Further wort is then forced in by hydraulic pressure, the contents of the cylinder are heated to 60° C. for a suitable length of time, next cooled to 0° C., the pressure being maintained, the liquid is drawn off and is ready, after the hop petals have been separated, for introduction into cooled wort or beer.—W. P. S.

*Brewers' worts; Rousing and mixing apparatus for* —. M. F. Chambers, Cork, and C. F. E. Skilton, Blackrock, Ireland. Eng. Pat. 101,363, Jan. 28, 1916. (Appl. No. 1377 of 1916.)

The apparatus comprises an open pan, perforated at its circumference, and connected at the bottom with a central pipe extending downwards. A rotating shaft passes down through the pipe and is provided at its lower end with a ribbed disc, above which is a covering disc attached to the lower end of the pipe. The central pipe is telescopic and, when the apparatus has been arranged at a suitable height in a vat, with its open top above the liquid level, the rotation of the shaft and ribbed disc draws the beer and yeast through the perforations and down the pipe, and distributes it horizontally round the bottom of the vat.—W. P. S.

*Musts; Preservation of* —. J. A. Dejeanne. Fr. Pat. 477,953, July 8, 1914.

THE organisms of grapes being confined in general to the outer surface of the fruit, musts not liable to spontaneous fermentation are obtained by sterilising the grapes, preferably by means of sulphurous acid, before pressing.—J. H. L.

*Starch; Liquefaction of* —, and use of fluorides in fermentations with moulds. H. Joucla, Fr. Pat. 478,972, May 18, 1915.

AFTER a preliminary cooking the amylaceous material, without addition of alkali, is liquefied by *Bact. Burdigalense* (see Fr. Pat. 474,948, this J., 1915, 1107); a few litres of culture suffice for 1000 kilos. of material. Before saccharification, which is effected by *Mucor Eloi* (*loc. cit.*) or a similar mould, in open vats, the mash is preferably heated for a short time to destroy adventitious infection, and a further culture of *Bact. Burdigalense* may be added together with the *Mucor*. Claim is also made to the use of sodium fluoride, which may be added after the first cooking, at the rate of 10 grms. per hectolitre of wort. The liquefying bacterium is not affected by this, and the *Mucor* as well as the yeast employed may be acclimatised to it. The characters of *Bact. Burdigalense* and *Mucor Eloi* are described. —J. H. L.

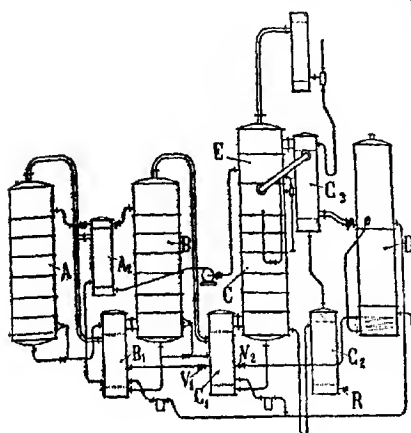
*Distillation and rectification of wines and fermented musts, methyl alcohol, etc.; Apparatus for the continuous* —. E. Barbet et Fils et Cie. First Addition, dated Apr. 25, 1914, to Fr. Pat. 470,242, June 10, 1913 (this J., 1915, 184).

MODIFICATIONS have been made in the apparatus previously claimed, in order to obtain rectified products free from esters. The vapours driven out of the wine in column, A (*loc. cit.*), undergo a preliminary purification by condensation, in an upper extension of the column, the lighter head-impurities passing out of the top of the column as vapour. The condensed liquid, still containing some esters, passes, together with a regulated quantity of caustic alkali, into the column, B, C, in which are intercalated some plates of relatively great depth to ensure that the liquid remains in this column for a sufficient time for the esters to be hydrolysed. Any ammonia or volatile bases produced during hydrolysis, are eliminated with other head-impurities from the top of column, B. The alkaline spirit leaving C, is neutralised on its way to the rectifier, K, L, by a regulated flow of sulphuric acid into the pipe, and small test-portions of the liquid can be taken from the plate of entry in K, to ascertain that the supply of acid is correct. A small quantity of caustic alkali is supplied continuously to the bottom plate in the upper extension of the column, A, and to the top plate of the de-alcoholising column, J, the object in both cases being to neutralise volatile acids from the wine, which would otherwise form esters on contact with vapours rich in alcohol. The rates of flow of alkali and acid to the parts of the apparatus mentioned, are easily observed and controlled by means of a special form of sight-glass.—J. H. L.

*Distillation of alcoholic and similar liquids; Process of multiple-effect* —. E. Barbet et Fils et Cie. Fr. Pat. 478,885, June 9, 1914, and First Addition thereto, dated Oct. 19, 1914.

DISTILLATION takes place simultaneously in a series of distilling columns, each working under a lower pressure than the preceding one. In the apparatus described there are three, each comprising a tubular heater and a plate column; the first is heated by steam, the second by the alcoholic

vapours from the first, and the third (at atmospheric pressure), by those from the second column. Each column has in communication with its lower end a tubular recuperator for the transfer of heat from the outflowing vinasses to



fresh wash. The whole of the fresh wash for re-charging the series passes first through the recuperator of the last column and also serves to condense the vapours from this column; it then passes through the recuperator of the second, or of the first column, or through a steam heater, according as it is destined to re-charge the third, second, or first column respectively. The phlegms from the first and second units, condensed in the second and third, are led into the top of the third column which contains some additional plates; the whole of the alcohol from the series is thus obtained finally from the third column, and in fairly concentrated condition. In a modified form of apparatus (see fig.) described in the Addition to the principal patent, there are no recuperators attached to the first two columns, A and B. The vinasses from each column pass through all the succeeding ones (or their tubular heaters, B<sub>1</sub>, C<sub>1</sub>) and then through the single recuperator, C<sub>2</sub>, in which they raise the temperature of fresh wash (entering at R) to 80°–85° C. The fresh wash is further heated almost to boiling, in C<sub>3</sub>, by condensing the vapours from the last column, and passes thence to a receptacle, E, at the top of the last column, C, where it is maintained in gentle ebullition to expel gas. From here the wash is transferred to the various columns, that destined for the first two being pumped through a tubular heater, A<sub>2</sub>, heated by a portion of the alcoholic vapours from A. The phlegms from the first two units, condensed in B<sub>1</sub> and C<sub>1</sub>, pass into the column of "épuration," D, and this column is heated by uncondensed portions of the same phlegms, which are regulated by the valves, V<sub>1</sub>, V<sub>2</sub>. The distillates from the last column, condensed in C<sub>2</sub>, also pass into the column, D, for "épuration."—J. H. L.

*Alcohol; Process and apparatus for the continuous rectification of — at the expense of vapours from the distilling column.* E. Barbet et Fils et Cie. Fr. Pat. 478,948, Oct. 19, 1914.

In a process of continuous distillation and rectification, the latter is effected at the expense of the heat of the vapours from the distilling column, by operating this column at a higher pressure

than the rectifier. Apparatus for applying the process to washes containing about 4% of alcohol is described. It comprises three columns, for distillation, "épuration" (removal of head products from phlegms), and rectification respectively. The rectifier works under ordinary pressure, and the distilling column under an excess pressure of at least 0.5 atm. The purifying and rectifying columns are heated by the alcoholic vapours from the distilling column, which are thereby condensed; these condensed phlegms then enter the purifying column, whence after removal of their head-impurities they pass into the rectifier. Fresh wash, after serving to condense vapours from the top of the rectifier, descends to a recuperator in which it is heated by vinasses from the distilling column, to such a temperature that on re-ascending to a receptacle at its former level it enters into gentle ebullition and is thus freed from gases. This receptacle is at such a height that the boiling wash flows from it into the top of the distilling column at the required pressure. In the distillation of washes containing only about 2% of alcohol the vapours contain more heat than is required for their rectification, and the excess can be made to operate a complementary distillation process under atmospheric pressure. A modification of the apparatus to suit these conditions is described.—J. H. L.

*Sparging; Process of —.* J. Schaefer, Assignor to Simon, Bühler, und Baumann, Frankfurt, Germany. U.S. Pat. 1,260,763, Oct. 10, 1916. Date of appl., Aug. 10, 1912.

SEE Eng. Pat. 17,028 of 1913; this J., 1914, 978.

*Column-stills; Process of heating —.* E. Guillaume, Paris. U.S. Pat. 1,199,371, Sept. 28, 1916. Date of appl., May 24, 1910.

SEE Fr. Pat. 403,385 of 1909; this J., 1910, 104.

*Manufacture of malt extract.* Eng. Pat. 16,887. See XIXA.

## XIXA.—FOODS.

*Lactose; Velocity of scission of — by the action of the "Bulgarian ferment."* H. G. Quagliariello and C. Ventura. Atti R. Acad. Lincei, 1916, [v], 25, i., 793–798. J. Chem. Soc., 1916, 110, i., 699.

THE conversion of lactose into lactic acid by *Bacillus bulgaricus* is not a unimolecular reaction, the value of the velocity constant showing a continuous diminution as the action proceeds. With two samples of milk containing different proportions of lactose, the action ceased in each case when the concentration of the lactic acid formed became about 0.270 gm.-mol. per litre, or about 2.5%, the bacteria apparently being incapable of vitality beyond this point. With an aqueous solution of lactose or with whey this maximal acidity has different values, but in all probability the hydrogen-ion concentration is the same in the three cases.

*Yeast, polished rice, and white bread; Nutritive value of — as determined by experiments on man.* C. Funk, W. G. Lyle, and D. McCaskey. J. Biol. Chem., 1916, 27, 173–191.

THE experiments indicate that the value of yeast as a source of protein is not very great; a large part of the yeast nitrogen has apparently no food value, it is assimilated badly, and causes a rise in the uric acid content of the blood. The amount

of nitrogen which would be fully adequate in the form of potatoes proves to be insufficient in the case of yeast; this also applies to white bread and polished rice. A positive nitrogen balance cannot be obtained by the addition of vitamins prepared from autolysed yeast by Seidell's method (U.S. Pat. 1,173,317; this J., 1916, 653).—W. P. S.

*Carotin*; *Toxicity of* —. H. G. Wells and O. F. Hedenburg. *J. Biol. Chem.*, 1916, 27, 213—216.

CAROTIN, the coloring matter of wheat flour and carrots, has no appreciable toxic action, and chlorination does not increase its toxicity. Quantities of 0.2 gm. of the substance injected into guinea pigs (weighing 245 to 265 grms.) had no effect on the health of the animals.—W. P. S.

*Growth-producing substance from sheep pancreas*; *Isolation of a* —. W. H. Eddy. *J. Biol. Chem.*, 1916, 27, 113—126.

SHEEP pancreas was extracted with alcohol containing 4% of HCl, the extracts were evaporated at a low temperature, the residue was dissolved in water, the solution filtered, the filtrate evaporated, then diluted with water, treated with sulphuric acid and phosphotungstic acid, the precipitate collected, decomposed by mixing with water and barium hydroxide, and the mixture filtered. After removing excess of sulphuric acid from the filtrate, the latter was evaporated, the residue treated with alcohol, and the alcoholic solution treated with alcoholic mercuric chloride solution. The precipitate obtained was decomposed with hydrogen sulphide, the mercury sulphide separated, and the purines in the solution then precipitated with silver nitrate and separated by filtration. The filtrate was treated with silver nitrate and barium hydroxide, the precipitate formed was decomposed with hydrogen sulphide, and the solution freed from barium, sulphuric acid, and chlorides. The resulting solution contained a substance which was capable of producing a marked increase in growth when administered to rats. The substance was precipitated by phosphotungstic acid and by colloidal hydrated aluminium silicate (Lloyd's reagent); it was not a protein, fatty substance, or a mixture of amino-acids.—W. P. S.

*Proteolytic action*; *An examination of certain methods for the study of* —. H. C. Sherman and D. E. Neun. *J. Amer. Chem. Soc.*, 1916, 38, 2199—2216.

EIGHT different methods have been comparatively investigated with commercial preparations of pepsin and trypsin. For the study of proteolytic activities solutions of casein form the most convenient substratum; in the case of pepsin 1 gm. of casein is dissolved in *M*/20-hydrochloric acid, the solution warmed, the enzyme added, and the volume made up to 100 c.c. After digestion, the undigested casein may be precipitated by pouring into 25 c.c. of 20% sodium sulphate solution. For experiments with trypsin, solutions of sodium caseinate of slight alkalinity are employed. One of the best quantitative methods of comparison is based on the determination of the total nitrogen by Kjeldahl's method in the filtrate after digestion and precipitation. The proportionality of the results to quantity of enzyme extends over a considerable range and the comparisons may be made either on the basis of the amount of digestion products produced in a given time (which should not be too long) or of the time required to render a given amount of nitrogen soluble, the latter method offering a longer range of accurate observations. Equally satisfactory comparisons are

obtainable by Van Slyke's amino-nitrogen determination method (this J., 1911, 771, 1135; 1915, 1110, 1275), with the added advantage that the proteolytic action may be followed in its more advanced stages, long after the total dissolved nitrogen has reached its maximum limit. Here also, it is important to confine the observations to reasonably short digestion periods of  $\frac{1}{2}$  to 1 hour, as over prolonged periods, differences in activity tend to become equalised. Another method of measuring the results of proteolysis which appears capable of giving useful indications, is the titration of the carboxylic acidity of the digestion products in presence of thymolphthalein as indicator; this method is somewhat less delicate than the determination of total nitrogen and about as delicate but not so regular as the amino-nitrogen method; the general trend of the indications is comparable with the total nitrogen method. Indirect methods, such as electrical conductivity and polarimetric methods, may be useful in certain cases, but are less desirable than methods based on direct chemical functions. Colorimetric methods, such as the biuret and the ninhydrin reactions, are of subordinate value for quantitative comparisons.—J. F. B.

*Humin formation*; *Reaction between amino-acids and carbohydrates as a probable cause of* —. M. L. Roxas. *J. Biol. Chem.*, 1916, 27, 71—93.

To obtain information on the structure and formation of humic substances, experiments were made to determine which amino-acids react with carbohydrates under certain conditions, whether different sugars behave alike towards the same amino-acid, and what group of the reactive amino-acids takes part in the reaction. It was found that under the conditions of the experiments alanine, leucine, phenylalanine, glutamic acid, and proline were not important factors in humin formation. The following amino-acids were responsible for humin formation, and when digested with 20% HCl plus sugar, the proportion of their nitrogen converted into humin-nitrogen was: tyrosine, 15.0; cystine, 3.1; arginine, 2.33; lysine, 2.02; histidine, 1.84; tryptophane, 71.0%. Xylose and levulose were, as a rule, more reactive than was dextrose. Arginine, histidine, and lysine reacted with sugars more readily in weak acid or aqueous solutions than in strong acid solution. Arginine, histidine, and tryptophane reacted with loss in reactivity of their amino nitrogen towards nitrous acid, but the amino group apparently remained intact in the humin from tyrosine and cystine. (See also Gortner, this J., 1916, 1030.)—W. P. S.

*Beans*; *Detection and determination of hydrocyanic acid in* —. L. Guignard. *Ann. Falsif.*, 1916, 9, 201—205.

BURMAH beans (*Phaseolus lunatus* species) imported into France for edible purposes were found to contain 0.025% of hydrocyanic acid, a quantity slightly in excess of the maximum quantity allowed. The isopurpurate reaction was used to detect the presence of hydrocyanic acid in these beans; 2 grms. of the powdered bean was mixed in a flask with 10 c.c. of water, and a strip of filter-paper dipped previously in a solution containing 1 gm. of picric acid and 10 grms. of sodium carbonate per 100 c.c. of water was suspended in the flask. An orange-red coloration developed on the paper within 12 hours when hydrocyanic acid was present. To determine the quantity of hydrocyanic acid, 20 grms. of the powdered beans was macerated with water for 12 hours, then steam distilled, and the distillate titrated with silver nitrate solution, potassium iodide being used as indicator.—W. P. S.

*Soya meal poisoning; Extracted*—— J. Board Agric., 1916, 28, 691—692.

SOYA beans, after the oil has been extracted with a solvent, are made into a meal or cake and used for cattle feeding; naphtha is usually employed for extracting the oil, but trichloroethylene has been used recently. The soya bean itself is not poisonous, nor is the meal prepared from beans which have been extracted with naphtha, but about four years ago a number of cases of cattle poisoning were caused by meal prepared from soya beans which had been extracted with trichloroethylene. Experimental proof was obtained that cattle were badly and in many cases fatally affected by this meal, but pigs and sheep were not affected. The symptoms appeared some days after the meal had been given. It would appear that trichloroethylene formed a poisonous substance by combination with some constituent of the meal, or that the trichloroethylene used was impure. Extracted soya bean meal is an excellent fodder, but it is inadvisable to use trichloroethylene for extracting the oil.—W. P. S.

*Cocoa; Determination of fat in*—— H. Kreis. Schweiz. Verein Anal. Chem., May, 1916. Chem.-Zeit., 1916, 40, 832.

ONE grm. of the cocoa is boiled for 15 mins. in a graduated tube with 20 c.c. of 1.5% hydrochloric acid, the mixture then cooled to 30° C., shaken for 5 mins. with ether, and centrifuged for 15 mins. (at least 1000 revolutions per min.). An aliquot portion (say 25 c.c.) of the ethereal solution is transferred to a nickel basin, the ether evaporated, the residue of fat heated for 10 mins. in a Soxhlet drying oven, and weighed.—W. P. S.

*Chicory; Detection of beetroot in*—— E. Collin. Ann. Falsif., 1916, 9, 271—272.

A PORTION of the suspected chicory is washed with Labarraque's solution (prepared by triturating 75 grms. of bleaching powder with 600 c.c. of water, added in two or three portions, filtering, adding a solution of 150 grms. of sodium carbonate in 400 c.c. of water, and again filtering) until all soluble colouring matter has been removed, and the particles are then examined under the microscope. If any particles of beetroot are present they will be seen to contain numerous black cells filled with crystals of calcium oxalate. The cells are oval or elongated and are more numerous near the ligneous vessels of the woody portion of the root. (See also this J., 1915, 568).—W. P. S.

*Calcium; Determination of*—— in the ash of forage plants and animal carcasses. S. B. Kuzirian. J. Amer. Chem. Soc., 1916, 38, 1996—2000.

THE following method is recommended as being more accurate and rapid than the so-called basic acetate method in general use:—From an acid solution of the ash the phosphorus is removed by precipitation as ammonium phosphomolybdate, and the calcium is precipitated as oxalate in the filtrate, either before or after the removal of the excess of molybdenum as sulphide. If the former alternative, which is probably preferable, be adopted, the oxalate precipitate is collected in a Gooch crucible, ignited to oxide in an electric furnace, dissolved in dilute hydrochloric acid, filtered, ammonium chloride and ammonia added to the filtrate, to precipitate iron and aluminium, and the calcium again separated as oxalate, the precipitate now being entirely free from molybdenum. If the second alternative be adopted the molybdenum in the filtrate from the phosphomolybdate precipitate is precipitated by digestion with colourless ammonium sulphide, and subse-

quent addition of 12% hydrochloric acid. The boiled filtrate is then ready for iron, aluminium, manganese, and calcium determinations. The results obtained by either procedure showed close agreement with the theoretical in the case of known solutions, and could be closely reproduced in analyses of plant and animal ashes.

—G. F. M.

*New methods in the wheat starch industry.* Goldbeck. See XV11.

*Formation of methylglyoxal and formaldehyde in glycolysis.* Sjollem and Kam. See XV111.

*Modification of the Pratt method for the determination of citric acid.* Willaman. See XX.

*Comparison of barbituric acid, thiobarbituric acid, and malonylguanidine as quantitative precipitants for furfural [from pentoses].* Dox and Plaisance. See XXXIII.

#### PATENTS.

*Beverage extracts; Manufacture of*—— J. L. Kellogg, Battle Creek, Mich., U.S.A. Eng. Pat. 14,134, Oct. 6, 1915.

A MIXTURE of ground algaroba (carob) bean, malt sprouts, and amylaceous materials is made into a dough which is moulded into loaves and these are kept at 140° to 160° F. (60° to 71° C.) for about 2 hours; the loaves are then dried and ground to a coarse powder. This powder is roasted, extracted with water, and the extract evaporated to form a dry powder. (See also Eng. Pats. 2472 of 1915 and 17,255 of 1915; this J., 1915, 1162; 1916, 940).—W. P. S.

*Beverage extract; Soluble*—— J. L. Kellogg, Assignor to Kellogg Toasted Corn Flake Co., Battle Creek, Mich. U.S. Pat. 1,199,387, Sept. 26, 1916. Date of appl., Oct. 23, 1915.

A SOLUBLE extract of a cooked and roasted mixture of about 3 parts of cereal flour, 2 of bran, and 3 of malt.—A. S.

*Milk or other liquids; Apparatus for the pasteurisation of*—— A. McCulloch and W. R. Walkey, London. Eng. Pat. 14,200, Oct. 7, 1915.

THE apparatus comprises a corrugated tray placed in the upper part of a heating bath. The liquid is delivered from an upper tank on to the corrugated tray, flows through the channels formed by the corrugations, and is discharged through an outlet pipe. The heating bath has a corrugated bottom and is provided with an expansion chamber.—W. P. S.

*Cheese or a cheese-like food product; Manufacture of*—— H. W. Crowe, Yelverton, Devon. Eng. Pat. 101,641, Jan. 3, 1916. (Appl. No. 27 of 1916.)

THE cheese curd is obtained by treating milk, skimmed milk, or heated milk with a culture of bacteria which produce but a small quantity of lactic acid. These bacteria exist in the atmosphere in the district of Christiania, Norway, and cultures may be prepared from milk curd imported from that district. If desired, the curd obtained may be mixed with a proportion of ordinary rennet curd.—W. P. S.

*Muscular flesh of animals of the bovine genus; Process for the preparation of the*—— which may be preserved afterwards by means of heat in appropriate receptacles. J. Balzani, Buenos Aires. Eng. Pat. 15,559, Nov. 4, 1915.

THE flesh is freed from fat, minced, sterilised in the



presence of water at 120°C., again minced, the liquid portion is separated and evaporated to a density of 7° B. (sp.gr. 1.05), the minced meat and the concentrated liquid are mixed, and the mixture is sterilised in hermetically closed receptacles.—W. P. S.

*Malt extract; Method of manufacture of* — S. H. Green, Lelant, and J. D. Opie, Hayle, Cornwall. Eng. Pat. 16,887, Dec. 1, 1915.

PERFORATED receptacles containing crushed malted cereal are placed in tanks arranged in steps and each provided with a heating coil. The containers are transferred successively from one tank to another after a suitable period of extraction, whilst the extracting liquid is transferred from tank to tank in the opposite direction. The arrangement is such that the nearly exhausted material is extracted in the upper tank with a weak liquor, and the material in the lowest receptacle and tank is extracted with an already strong liquor which has passed in succession through the series of tanks. The temperature of the liquids in the tanks is so graduated in regular steps that the liquid in the top tank is nearly boiling whilst that in the last tank is at about 120° F. (49° C.). The extract is discharged from the last tank and concentrated under reduced pressure.—W. P. S.

*Gelatinous substances; Method for the production of solid* — Solid gelatinous [food] product. P. Askenasy, Karlsruhe, Assignor to A.-G. für Chem. Prod. vorm. H. Scheidemandel, Berlin, Germany. U.S. Pats. 1,201,132 and 1,201,133, Oct. 10, 1910. Date of appl., Oct. 19, 1915.

SEE Eng. Pat. 100,392 of 1916; this J., 1916, 855. The process may be applied to the manufacture of food products consisting of small globules containing a food substance mixed with an animal gelatinous substance.

## XIXB.—WATER PURIFICATION; SANITATION.

*Hydrogen sulphide; Determination of* — in water. L. W. Winkler. Z. angew. Chem., 1916, 29, 383—384.

VERY small quantities of hydrogen sulphide in water may be determined colorimetrically (this J., 1913, 957). The following method is recommended for larger quantities:—The water is collected in a glass-stoppered bottle of 500 c.c. capacity, containing 10—20 grms. of coarse marble which has previously been washed with dilute hydrochloric acid. For the determination, the stopper is removed and replaced by another carrying a bulb tube, a side tube from which leads first to a U-tube containing cotton wool and then to an absorption bulb containing 50 c.c. of freshly-made bromine water which must be free from acid. A stopper in the upper end of the bulb tube carries the stem of a separating funnel in which is placed 50 c.c. of 18% hydrochloric acid. The acid is discharged in three portions: half to start the reaction, one quarter after the lapse of an hour, and the remainder after another hour. The hydrogen sulphide is oxidised to sulphuric acid by the bromine, and after evaporating until the excess of bromine and the hydrobromic acid are expelled, the sulphuric acid may be titrated with N/100 borax, using methyl orange as indicator, or, preferably, the bromine alone may be expelled by boiling, and the mixed hydrobromic and sulphuric acids titrated with borax. A method for determining the strength of hydrogen sulphide water consists in placing 100 c.c. of N/10 potassium permanganate solution and 1 grm. of

pure sodium hydroxide in a glass-stoppered flask of 250 c.c. capacity, weighing the flask with its contents, adding a few c.c. of the water to be tested, and re-weighing. After an hour the solution is acidified with sulphuric acid, treated with potassium iodide, and titrated with N/10 sodium thiosulphate solution. 1 c.c. of N/10 potassium permanganate solution = 0.4263 mgrm. H<sub>2</sub>S. It is necessary to have an excess of permanganate, and if the acidified solution is green the test must be repeated with a smaller quantity of the sample.—A. B. S.

*Sewage disposal; Experiences with the Emscher tank and similar methods of* — K. Thurmann and A. Reichle. Mitt. Kgl. Landesanst. f. Wasserhyg., 1914, 18, 48. Chem.-Zeit., 1916, 40, Rep., 347—348.

THE chief difficulties encountered in the Emscher tank (see Fowler, this J., 1911, 1346) and similar methods of sewage disposal arise from the formation of acid sludge in the sludge-decomposing chambers, the separation of sludge as a floating layer, and frothing. Sludge from a properly working Emscher tank has a deep black colour due to ferrous sulphide, an alkaline reaction, and a characteristic, not unpleasant odour, and drains easily; the effluent has no putrid odour and contains ammonia and free carbon dioxide. When, however, the sewage contains an excessive quantity of carbohydrates, and relatively small quantities of nitrogen compounds and ammonia or other bases, fermentation frequently occurs instead of putrefaction, and yellow to black, acid sludge is obtained, which has an unpleasant smell and drains badly. To obtain sludge of satisfactory quality, effective agitation, by means of stirrers and by blowing, is required; the ratio of sludge to sewage in the sludge-decomposing chamber should be about 1:2. Limited quantities of moderately hard water or of lime may be added to the sewage to increase the acid-fixing power. The separation of sludge as a floating layer occurs most frequently when the sludge-decomposing chambers first come into operation, and one of the chief causes is insufficient mixing of the sludge and sewage. The floating layer should be broken at intervals by pumping sewage on to it, by mechanical stirring, or by lowering the liquid level in the settling or decomposing chambers.—A. S.

*Preparation of diphenylamine-sulphuric acid reagent.* Tönies. See XXIII.

### PATENTS.

*Waters containing iron in organic combination; Purification of natural* — Stadtgemeinde Breslau, and W. Wagenknecht, Breslau. Ger. Pat. 294,098, Nov. 5, 1913.

THE water to be purified is mixed with water containing iron in inorganic combination, and the mixture is treated with a quantity of lime water equivalent to the inorganic iron, and then passed over a trickling filter. The colloidal ferrous hydroxide first formed is oxidised to ferric hydroxide, and precipitated, and carries down with it the iron present in organic combination.—A. S.

*Tetramurpic sulphate; Preparation of* —, and its use as a fungicide. Soc. des Prod. Agricoles Mouillants à l'Adhésol. First Addition, dated June 22, 1914, to Fr. Pat. 476,512, Apr. 24, 1914 (this J., 1916, 67).

PENTA-CUPRIC sulphate, CuSO<sub>4</sub>·4CuO, 6H<sub>2</sub>O, is obtained by operating under the conditions described in the main patent, if the strength of the copper solution is kept low in comparison with



the high concentration of the sodium carbonate, but the copper sulphate must always be kept in excess. By replacing the free alkali or carbonate by an alkaline-earth carbonate, e.g., calcium carbonate, the copper sulphate being kept in excess during the preparation, a tetracupric sulphate,  $\text{CuSO}_4 \cdot 3\text{CuO} \cdot 4\text{H}_2\text{O}$ , may be obtained, or, with a less proportion of calcium carbonate, a basic cupric sulphate of the formula,  $2\text{CuSO}_4 \cdot 3\text{CuO} \cdot 5\text{H}_2\text{O}$ , may be obtained.—B. N.

*Purifying water containing mineral salts.* P. Münzer, Braunsfeld, Germany, Assignor to Reiser Automatische Water Purifying Co. U.S. Pats. 1,199,098 and 1,199,099, Sept. 26, 1916. Dates of appl., Jan. 28, 1910, and Mar. 24, 1916.

SEE Fr. Pat. 411,532 of 1910; this J., 1910, 974.

*Sterilisation of fluids; Apparatus for the—*. W. R. Walkey, London. U.S. Pat. 1,199,642, Sept. 26, 1916. Date of appl., Apr. 8, 1915.

SEE Eng. Pat. 14,680 of 1914; this J., 1914, 1221.

*Water and other liquids; Apparatus for treatment of—by ultra-violet rays.* V. Henri, Paris, and A. Helbronner and M. von Recklinghausen, Suresnes, France, Assignors to The R.U.V. Co., Inc. U.S. Pat. 1,200,940, Oct. 10, 1916. Date of appl., Nov. 10, 1913.

SEE Eng. Pat. 20,436 of 1910; this J., 1911, 1229.

## XX.—ORGANIC PRODUCTS; MEDICINAL SUBSTANCES; ESSENTIAL OILS.

*Ipecacuanha; Alkaloids of—*. P. Karrer, Ber., 1916, 49, 2057—2079. (See also this J., 1914, 764.)

THE empirical formula,  $\text{C}_{22}\text{H}_{33}\text{O}_5\text{N}$ , and  $\text{C}_{22}\text{H}_{33}\text{O}_5\text{N}_2$ , attributed by Carr and Pyman to emetine and cephaeline respectively, are confirmed when the analysis is made on the substances dried at  $110^\circ\text{C}$ . Emetine contains four and cephaeline three methoxyl groups, and when demethylated with hydriodic acid yield compounds containing iodine which can be removed by shaking the alcoholic solutions with silver oxide, the same substance emetoline, m.pt.  $205^\circ\text{C}$ ., being obtained in each case. Cephaeline on methylation with sodium m. thioxide and dimethyl sulphate or with diazomethane is converted into emetine and can be converted similarly into higher homologues such as ethyl-emetine (emetethylene), m.pt.  $68^\circ\text{—}71^\circ\text{C}$ ., propyl-emetine (emetpropylene), m.pt.  $58^\circ\text{—}60^\circ\text{C}$ ., and allyl-emetine (emetallylene) which possess similar physiological properties to emetine but in a gradually diminishing degree. Emetine on complete methylation yields a well-crystallised salt,  $\text{C}_{25}\text{H}_{38}\text{N}_2\text{O}_4(\text{CH}_3)_2(\text{H}_2\text{I})$ , which gives the corresponding base with silver oxide. This base on distillation in a vacuum gives a new base, anhydrotetramethylemetine,  $\text{C}_{25}\text{H}_{37}\text{O}_4(\text{NCH}_3)_2(\text{NCH}_2)$ , without loss of nitrogen. This base on complete methylation with methyl iodide and treatment with silver oxide yields after distillation in a vacuum a base  $\text{C}_{25}\text{H}_{37}\text{O}_4\text{N}(\text{CH}_3)_3$ , together with trimethylamine. From this the conclusion is drawn that one of the nitrogen atoms in emetine is in a simple ring whilst the other forms part of two ring systems. Emetine on oxidation with an alcoholic solution of iodine yields dehydro-emetine iodide, which forms golden-yellow needles, m.pt.  $177^\circ\text{—}179^\circ\text{C}$ ., similar to the products obtained by the oxidation of hydrogenated isoquinoline derivatives such as canadine and corydaline.—T. C.

*Cryptopine and protopine.* W. H. Perkin, jun. Chem. Soc. Trans., 1916, 109, 815—1028.

CRYPTOPINE,  $\text{C}_{21}\text{H}_{27}\text{O}_5\text{N}$ , occurs in opium in very minute proportions (5 oz. of the hydrochloride obtained from 10,000 lb. of opium) and is isolated after the separation of the morphine and thebaine. Hitherto the only direct constitutional clue was the formation of *m*-hemipinic acid on oxidation with permanganate, indicating a dimethoxybenzene nucleus. The presence of a methylenedioxybenzene or piperonyl nucleus was regarded as probable and is now confirmed. Cryptopine combines readily with methyl sulphate yielding the methosulphate; when this is reduced with sodium amalgam in boiling acid solution, it is converted into tetrahydromethylcryptopine,  $\text{C}_{21}\text{H}_{29}\text{O}_5\text{N}$ . By the action of acetyl chloride on this, water is eliminated yielding anhydrotetrahydromethylcryptopine, and this latter, on oxidation with dry permanganate in acetone solution, yields a syrupy base (A), an aldehyde (B), m.pt.  $74^\circ\text{—}75^\circ\text{C}$ ., an acid (C), m.pt.  $153^\circ\text{C}$ ., an acid (D), m.pt.  $217^\circ\text{C}$ ., and *m*-hemipinic acid. The syrupy base is the *N*-methyl derivative of 4,5-dimethoxy-2- $\beta$ -methylaminoethylbenzaldehyde and therefore represents the dimethoxybenzene nucleus with a methylated side chain of  $\text{CH}_2\text{CH}_2\text{N}(\text{CH}_3)$ . The acid (C) is the *N*-formyl derivative of a similar benzoic acid and belongs to the same portion of the cryptopine molecule. The aldehyde (B) and acid (D) represent the methylenedioxybenzene nucleus; the aldehyde is a methylpiperonal, yielding on oxidation a methylpiperonylic acid identical with (D), and it has been characterised as 5,6-methylenedioxy-*o*-tolu aldehyde. Combining products (A) and (B), on the assumption that their aldehyde groups are produced by the oxidation of an ethylene bond, the formula of anhydrotetrahydromethylcryptopine may be reconstructed, and the addition of  $\text{H.OH}$  at the ethylene bond gives that of tetrahydromethylcryptopine, with  $\text{CH}(\text{OH})\text{CH}_2$  joining the two nuclei. This link is also present in dihydrocryptopine and is formed by the hydrogenation of  $\text{CO.CH}_2$ , or its enolic equivalent  $\text{C}(\text{OH})\text{:CH}$  in cryptopine itself, the  $\text{CO}$  being attached to the dimethoxybenzene and the  $\text{CH}_2$  to the methylenedioxybenzene portion. To complete the structure of cryptopine, the nitrogenous side-chain (*supra*) of the dimethoxybenzene nucleus is joined up to the methyl group of the methylpiperonyl nucleus, with subtraction of  $\text{H}$  and  $\text{CH}_2$ . Thus the two nuclei are united in cryptopine by a closed chain of nine carbon atoms and one nitrogen ( $\text{N}^+\text{CH}_2$ ), which becomes ruptured in the hydrogenation of the methosulphate, whereby the *N* becomes terminal in taking up a second  $\text{CH}_2$ . Cryptopine cannot be resolved into optically active components and contains no asymmetric carbon atom; it does not yield an acetyl derivative and, in spite of the  $\text{CO.CH}_2$  group, it does not combine with hydroxylamine or semicarbazide, which is explained by steric hindrance. From the enolic form of cryptopine are derived by the action of strong acids well defined quaternary salts of isocryptopine in which the hydroxyl of the enol migrates to the  $\text{NCH}_2$ , and the dihydroisoquinoline ring is closed; the sparingly soluble disulphate is most characteristic. By the action of dilute nitric acid under certain conditions, cryptopine yields a mixture of nitro-cryptopine and dibasic cryptopidic acid in which the piperonyl nucleus is oxidised away; strong nitric acid yields two dinitro-cryptopines. Dihydro-cryptopine is formed by reduction with sodium amalgam and boiling dilute sulphuric acid and yields quaternary chlorides of isodihydrocryptopine on digestion with acetyl or phosphoryl chloride. With methyl alcoholic potassium hydroxide, these chlorides lose  $\text{HCl}$ , giving two anhydro-dihydrocryptopines, from which are derived by exhaustive methylation, first methylisohanhydro-

dihydrocryptopine and then  $\alpha$ - and  $\beta$ -isocryptopidols,  $C_{10}H_{16}O_3$ , with elimination of the nitrogen as trimethylamine. This series of reactions is closely duplicated in the berberine series. By the methylation of cryptopine, two methylcryptopines may be obtained according to whether the rupture of the ring takes place on one side of the nitrogen atom or the other; both yield cryptopidol and anhydrocryptopidol on exhaustive methylation. Anhydrocryptopine is formed by the action of methyl alcoholic potassium hydroxide on isocryptopine chloride; this compound has the closed dihydroisoquinoline ring characteristic of isocryptopine through the union of the nitrogen with the enolic group, but the remainder of the original ten-member ring of cryptopine forms an open side chain  $\cdot CH:CH_2$ . Anhydrocryptopine, from a constitutional point of view, is one of the most interesting members of the cryptopine series, owing to its extraordinary reactivity, and forms the starting point of a large number of important derivatives. One of the most striking series of transformations is its conversion by strong hydrochloric acid into the *epicryptopines*, in which the  $CO.CH_2$  group is inverted as compared with cryptopine. By the subsequent action of phosphoryl chloride a range of intensely coloured *epicryptopirubin* salts is obtained. *Protopine*,  $C_{10}H_{15}O_2N$ , is an alkaloid also present in opium but most conveniently extracted from the root of *Dicentra spectabilis*. Protopine shows a complete analogy with cryptopine in the most characteristic transformations now elucidated and there can no longer be any doubt that these alkaloids are intimately related in constitution, in such a manner that the two methoxy groups in cryptopine are replaced by a methylenedioxy group in protopine.—J. F. B.

*Camphor oil of high boiling point; Constituents of*—  
K. Kafuku. Kogyō-Kwagaku-Zasshi  
(J. Chem. Ind., Tokyo), 1916, 19, 815—822.

CAMPHOR oil distilled by the Monopoly Bureau, Formosa, had the following characters:—Sp.gr. at 15° C., 0.9805;  $n_D^{20}$  = 1.5035; ester value, 0.66; ester value after acetylation, 126; and acid value, 3.14. The oil contained lauric acid, and a substance,  $C_{14}H_{26}O_2$ , probably a lactone of an aliphatic hydroxy acid. The fraction of highest boiling point contained piperonylic acid, which had possibly been formed by oxidation of the saffrol during the distillation. A tricyclic sesquiterpene alcohol was also isolated.—C. A. M.

*Optically active diaminoglycerol; Synthesis of*—  
E. Abderhalden and E. Eichwald. Ber., 1916, 49, 2095—2103.

ALLYL bromide, prepared by passing hydrogen bromide into allyl alcohol, is added gradually to sodium methoxide, the resulting allylmethylether distilled off below 62° C., dissolved in chloroform, and the theoretical quantity of bromine added, with ice-cooling, to convert it into dibromoallylmethylether,  $CH_2Br.CHBr.CH_2OCH_3$ . The latter is then converted into  $\alpha\beta$ -diamino- $\gamma$ -methoxyglycerol by heating for 2 days at 90°—100° C. under pressure with a saturated alcoholic solution of ammonia, the diaminomethoxyglycerol being separated by adding solid potassium hydroxide, removing the alcohol by heating in a salt bath, and distilling off the crude diamine in a vacuum. The yield of diaminomethoxyglycerol is only 5 to 8%, the chief products being high-boiling, unsaturated, amino compounds.  $\alpha\beta$ -Diamino- $\gamma$ -methoxyglycerol gives a well-crystallised salt with bromocamphorsulphonic acid which after recrystallising ten times and then distilling with potassium hydroxide yields *d*- $\alpha\beta$ -diamino- $\gamma$ -methoxyglycerol,  $[\alpha]_D^{20}$  = + 8° 19 in

aqueous solution. The *l*- $\alpha\beta$ -diaminomethoxyglycerol can be recovered as hydrobromide from the mother liquors by passing in hydrogen bromide. *i*-Diaminomethoxyglycerol on heating with concentrated hydrobromic acid is converted into *i*-diaminoglycerol dihydrobromide, m.pt. 198° C., whilst the *d*- and *l*-modifications are similarly converted into *d*- and *l*-diaminoglycerol dihydrobromides,  $[\alpha]_D^{20}$  = + 5° 20 and - 2° 51 respectively. On heating *i*- and *d*- $\alpha\beta$ -diaminoglycerol dihydrobromide for 4 to 6 hours in a sealed tube with a saturated solution of hydrobromic acid at 140°—150° C., they are converted respectively into *i*- $\alpha\beta$ -diamino- $\gamma$ -bromoglycerol dihydrobromide and *d*- $\alpha\beta$ -diamino- $\gamma$ -bromoglycerol dihydrobromide,  $[\alpha]_D^{20}$  = + 7° 27.—T. C.

*Citric acid (in fruit juices, etc.); Modification of the Pratt method for the determination of*—  
J. J. Willaman. J. Amer. Chem. Soc., 1916, 38, 2193—2199.

WITH Pratt's method, based on the oxidation of citric acid to acetone and precipitation of the latter as mercuric compound, considerable difficulty is experienced in obtaining concordant results. The author has modified the original method in many important respects and recommends the following procedure as satisfactory:—The pectins are separated by adding to the juice twice its vol. of 50% alcohol; the precipitate is filtered off with the aid of the pump, sucked as dry as possible, and washed twice with 65% alcohol. The filtrate is diluted to contain approximately 30% of alcohol by vol., and 5 c.c. of a 10% solution of barium acetate in 30% alcohol slowly added. The barium citrate is collected on asbestos in a Gooch crucible, washed once with 30% alcohol, and dried in the oven. It is then dissolved with hot 6% phosphoric acid, using three portions of 20 c.c. each, followed by hot water; filtrate and washings should amount to about 100 c.c. The solution is transferred to a 200 c.c. distillation flask connected with a spiral condenser and with a reservoir of potassium permanganate (0.5 grms. per litre) controlled by a screw pinch-clip. The adapter of the condenser dips into 40 c.c. of Deniges' solution (this J., 1899, 179); the citrate solution is briskly boiled over a naked flame, and the permanganate introduced at the rate of 20—25 drops in 10 secs. When a deep pink colour has persisted for 2 mins. the reaction is finished; if it is necessary to add more water, the addition of permanganate must be stopped a little while before the distillation is interrupted. The distillate is made up to 300 c.c. and boiled gently under a reflux condenser for 45 mins.; if the distillate is over 300 c.c., it is important that more of the Deniges' solution be added at the rate of 15 c.c. for each 100 c.c. excess of distillate. The solution is filtered hot through paper, the precipitate washed twice by decantation with hot water, and the filter thoroughly washed. The precipitate in the flask and on the filter is dissolved in hot 5% hydrochloric acid, the solution and washings are collected in a 100 c.c. flask, nearly neutralised with 10% sodium hydroxide, and made up to 100 c.c. This solution is titrated against 10—15 c.c. of standard potassium iodide at 28.0218 grms. per litre, 1 c.c. of which is equivalent to 2.0 mgrms. of citric acid.—J. F. B.

*Nitriles; Studies in the preparation of*—  
Preparation of aliphatic nitriles. G. D. van Epps and E. E. Reid. J. Amer. Chem. Soc., 1916, 38, 2120—2128.

ALIPHATIC as well as aromatic nitriles are readily prepared with good yields by distilling mixtures of well dried heavy metal salts of the acids with a

light excess of lead or other thiocyanate. As a rule, the zinc salt of the acid mixed with lead thiocyanate gives the best results. The use of a large excess of the thiocyanate or of reduced pressure in distillation shows no material advantage. For the preparation of acetonitrile, a mixture of 1 part of dried zinc acetate and 2 parts of lead thiocyanate is heated in a glass retort until no more distillate comes over; the residue consists of a mixture of zinc and lead sulphides. The crude distillate is mixed with half its volume of water, saturated with solid potassium carbonate or ammonia gas, and the nitrile separated and fractionated. In dealing with larger quantities an iron retort may be used, but the product is generally slightly coloured. For small quantities better yields may be obtained by distilling from a glass tube, 300 mm. long and 22 mm. in diameter, fitted into a hole bored in a brass block 50 mm. square and 300 mm. long; the block is heated by two Bunsen burners and the heat is thereby applied slowly and uniformly to the reaction mixture. Generally, higher yields are obtained of nitriles of higher molecular weight. In the case of isovaleronitrile, 80% of the theoretical quantity was recorded; hydrocinnamonnitrile was also obtained with specially high yields. Manganese salts of the acids, particularly manganese acetate, may also be employed with advantage but are not so generally available as the zinc salts; in certain cases cuprous thiocyanate may be employed instead of lead thiocyanate.—J. F. B.

*Nitriles; Studies in the preparation of*—III. The catalytic preparation of nitriles. G. D. van Epps and E. E. Reid. J. Amer. Chem. Soc., 1916, 38, 2128—2135.

WHEN acetic acid vapour mixed with a moderate excess of ammonia is passed over alumina or thorina heated at 500°C., acetonitrile is formed, with yields which may amount to 85% of the theoretical quantity. This reaction forms the basis of a continuous process for the preparation of acetonitrile in large quantities, requiring very little attention. The best yields are obtained with glacial acid of approximately 100% strength, introduced into the reaction tube with ammonia gas drawn directly from a cylinder. The catalyst is prepared by soaking pumice stone, in pieces 3—5 mm. in diam., in a strong solution of aluminium sulphate, treating with ammonia solution, and washing. The prepared pumice is dried in the reaction tube in a current of ammonia gas. Thorina gives slightly inferior results to alumina and is not employed on the practical scale. The apparatus consists of a very thick-walled copper tube, 762 mm. long and 32 mm. bore, heated by long burners. The acid is run in through a brass tube containing a trap to prevent the exit of vapours; this tube is carried to about 80 cm. inside the copper tube, so that the acid is vaporised on entering; it is surrounded by a wider but shorter tube through which the ammonia is introduced, so that the acid enters directly into an atmosphere of ammonia at the temperature of reaction. The products issuing from the copper tube pass through a condenser into a receiver, beyond which is a flask containing acid for the absorption of the excess of ammonia. The temperature of the copper tube is indicated by an apparatus which measures its expansion; the most favourable range is 500°—530°C. The acetic acid enters the trap-tube at the rate of about 1 drop per sec., and the ammonia is regulated so that white vapours fill about one-half of the condenser tube. The liquid in the receiver generally forms two layers, the acetonitrile being concentrated in the upper and ammonium acetate in the lower layer. After a certain time, the catalyst becomes inefficient and covered with a

black deposit; the yield depends on the activity of the catalyst and is affected by trifling differences in the method of preparation.—J. F. B.

*New method for purification of colloidal solutions.* Wegelin. See I.

*Colours produced by resorcinol in solutions of certain salts and their use for the detection of resorcinol in presence of other phenols.* Krauskopf and Ritter. See III.

*Formation of methylglyoxal and formaldehyde in glycolysis.* Sjollesma and Kam. See XVIII.

*Reactions of peroxidase purified by ultrafiltration.* Bach. See XXIII.

#### PATENTS.

*Anhydrides of aliphatic acids; Process for the manufacture of*—H. Dreyfus. Fr. Pat. 479,651, June 30, 1914.

ANHYDRIDES of aliphatic acids may be prepared by distilling a dry intimate mixture of a pyrosulphate with a salt of the appropriate acid, e.g., distillation of a mixture of sodium pyrosulphate and sodium acetate yields acetic anhydride. Diluents such as acetic anhydride or acetic acid may be employed.—F. Sp.

*Acetic acid and acetaldehyde; Manufacture of*—from acetylene. H. Dreyfus. Fr. Pat. 479,658, Dec. 23, 1914. Under Int. Conv., Nov. 30, 1914.

IN the manufacture of acetaldehyde by the combination of water with acetylene in the presence of a mercury salt, a liquid medium is employed in which the mercury salt is soluble, e.g., acetic acid, or which has a greater solvent power for acetylene than water, e.g., acetone. In order to oxidise the acetaldehyde to acetic acid, oxidising substances are added, e.g., hydrogen peroxide, perborates, percarbonates, permanganates, bichromates, ozone, etc., or the oxidation may be effected by oxygen or air, with or without catalysts such as cerium oxide, vanadium pentoxide, cerium salts, copper acetate, manganates, manganese or copper nitrate, platinum or palladium sponge, etc. *Example:* Into a mixture of 400 parts of glacial acetic acid, 100 parts of water, 50 parts of mercuric nitrate, and 10 parts of cerium oxide at 50°—100°C., is passed 130 parts of acetylene and 80—100 parts of oxygen. Acetic acid is produced continuously, and may be drawn off at intervals and distilled, the residue being returned to the reaction vessel.—F. Sp.

*Ethers [e.g., ethyl ether, or esters]; Apparatus for the continuous production of rectified*—E. Barbet et Fils et Cie. Fr. Pat. 479,435, Dec. 1, 1914.

THE apparatus is described more particularly for producing ethyl ether by the action of sulphuric acid or alcohol. Sulphuric acid is fed into the top compartment of a plate tower containing, for example, twelve sections, each of which is heated by a coil to a suitable temperature. Alcohol is introduced into the fourth section from the bottom, where it meets the descending stream of hot sulphuric acid and is partially converted into ether. A mixture of ether and alcohol vapours rises through the tower, and by contact with the acid in each section the conversion of the alcohol to ether becomes more and more complete. The three lowest sections remove alcohol and ether from the dilute sulphuric acid which reaches the bottom of the tower, where it is run off continuously by means of a siphon tube. The ether vapour

from the top of the tower passes into a rectifying column, where alcohol is condensed and returned to the fourth section of the tower. The ether passes to a condenser and is condensed and collected. The apparatus may also be used for the preparation of esters, e.g., ethyl acetate.

—F. Sp.

*a-Methylcoumarones; Preparation of*—. Farbenfabr. vorm. F. Bayer und Co. Ger. Pat. 293,956, Feb. 5, 1915. Addition to Ger. Pat. 279,884 (this J., 1915, 451).

By the action of alkalis on  $\alpha$ -halogen- $\alpha$ -allylphenols,  $\alpha$ -methylcoumarones are formed, suitable for pharmaceutical purposes and for use in perfumery.—A. S.

*2-Phenylquinoline-4-carboxylic acid and its substitution products; Manufacture of amino-derivatives of*—. Farb. vorm. Meister, Lucius, u. Brüning. Ger. Pat. 294,159, July 23, 1914. Addition to Ger. Pat. 287,904 (this J., 1916, 198).

**AMINO-DERIVATIVES** of 2-phenylquinoline-4-carboxylic acid or its substitution products are prepared by condensing mono-acyl derivatives of phenylenediamines, their homologues or substitution products with benzaldehyde, its homologues or substitution products, and pyruvic acid, and saponifying the resulting N-acyl compounds. (See also Ger. Pat. 288,865; this J., 1916, 384.)

—A. S.

*Manufacture of malt extract*. Eng. Pat. 16,887. See XIXA.

## **XXI.—PHOTOGRAPHIC MATERIALS AND PROCESSES.**

*Proportional [photographic] reducers*. K. Huse and A. H. Nietz. J. Franklin Inst., 1916, 182, 632—33. From Eastman Kodak Research Laboratory, Comm. No. 39. (See also Brit. J. Phot., 1916, 580—582.)

By density measurements before and after reduction it was found that most photographic reducers have the greatest proportional effect on low densities, this being most marked with Farmer's ferricyanide and "hypo" reducer. Only ammonium persulphate has a proportionally greater effect on the higher densities. A mixture of persulphate and permanganate, suggested by Deck, has an effect more nearly proportional to the density, and after trying various proportions, the authors recommend the following as the best: 1 part of a solution containing 0.025% potassium permanganate and 1.5% of 10% sulphuric acid to 3 parts of a solution containing 2.5% ammonium persulphate. The exact effect, however, is dependent both on the plate used and on the developer.

—B. V. S.

*Photochemical decomposition of certain acid chlorides*. Olivier. See III.

*Influence of strong salt solutions on the spontaneous oxidation of pyrogallol, ferrous sulphate, and laevulose*. MacArthur. See XXIV.

### **PATENTS.**

*Photographic colour records, and method of and means for producing them*. Panchromotion, Inc., Assignees of C. Raleigh and W. van D. Kelley, Jersey City, U.S.A. Eng. Pat. 14,225, Oct. 7, 1915. Under Int. Conv., Oct. 7, 1914.

In taking cinematograph negatives by successive

exposures through different coloured screens, each screen is provided with a section passing white, or approximately white, light, so that each negative is due partly to a colour exposure and partly to a white light exposure. The proportion of white light may vary with each screen, and it may be modified by an extra screen to cut out ultra-violet or to correct an artificial light. It is preferred to arrange that the white light exposure shall come in the middle of the coloured light exposure. The time of exposure is reduced and the times for the different screens are made equal. It is claimed that a reproduction is obtained with more detail and more delicate colouring than is usual.—B. V. S.

*Flashlight powders; Production of smokeless and odourless*—. E. Wadkind, Strassburg, and Geka-Werke Offenbach Dr. G. Krebs Ges., Offenbach. Ger. Pat. 293,908, Mar. 24, 1914.

FLASHLIGHT powders which burn without smoke or odour, and permit of photographing rapidly moving objects, are obtained by mixing finely-divided rare earth metals, such as zirconium, thorium, or titanium, with their nitrates or perchlorates.—A. S.

## **XXII.—EXPLOSIVES; MATCHES.**

*German explosives industry*. Engineering, Nov. 2, 1916.

AN all-round increase of capital is noted in the German explosives industry. Thus the Verein. Köln-Rottweiler Pulverfabriken is to increase its capital from 16,500,000 marks to 33,000,000 marks. The Rheinisch-Westfälische Sprengstoff A.-G. is also doubling its existing capital of 6,000,000 marks, and the Siegen Dynamite Company, of Cologne, is increasing its capital of 300,000 marks in the same proportion. The Köln-Rottweiler company paid a dividend of 35% in 1915, whilst the Dynamit A.-G. vorm. A. Nobel und Co., of Hamburg, with a capital of 36,000,000 marks, paid 20%.

*Trinitrotoluene and tetranitromethylaniline; Sensitiveness to detonation of*—. G. B. Taylor and W. C. Cope. U.S. Bureau of Mines. Tech. Paper 145. Chem. News, 1916, 114, 203—204, 211—212.

Tests were made to determine the minimum charges of fulminate-chlorate (90:10) primer required to cause complete detonation of mixtures in varying proportions of trinitrotoluene and tetranitromethylaniline. The mixtures were made by fusing the two substances together. The cooling curves for different rates of cooling gave no indication of the formation of an unstable compound as concluded by Guia (this J., 1915, 934). The "sand-test" of Storm and Cope (this J., 1916, 1132) was used:—Exactly 0.4 gm. of the explosives or the mixtures was placed in a copper shell 5 mm. in diameter, and slightly pressed with a flat-headed glass rod. The primer (90% mercury fulminate and 10% potassium chlorate) was placed above the explosive, and a thin copper reinforcing cap (9 mm. long with 2.3 mm. perforation) was inserted and pressed down into the shell for 1 min. under a pressure of 200 atmos. A short length of fuse was introduced and the detonator was fired in the cylindrical steel sand bomb. In cases of incomplete detonation part of the charge unexploded was found in the sand. The minimum charge was taken as being that which produced five complete detonations and no failures. The following results were thus obtained:—

Trinitrotoluene (T.N.T.)	Tetranitromethyl- aniline (Tetryl)	Smallest weight of primer causing com- plete detonation.
%	%	gram.
100	0	0.25
90	10	0.22
80	20	0.21
50	50	0.20
0	100	0.19

Mechanical mixtures of the two finely powdered explosives gave the same results as mixtures prepared by fusion, so that it is unnecessary to assume the existence of a compound to account for the increased sensitiveness of the mixtures. Analogous detonators with 0.4 grm. of base charge and 0.32 of primer were stored over water and tested at intervals. Pure T.N.T. failed when the detonator had absorbed 0.003 grm. of moisture; a mixture containing 10% tetryl detonated when the moisture was 0.0037 grm., but failed when it reached 0.0048 grm.; a mixture containing 50% tetryl detonated when the moisture was 0.0048 grm., but failed at 0.0055 grm., and the pure tetryl still detonated with a moisture absorption of 0.0062 grm. Lead azide ( $\text{PbN}_2$ ) detonates tetryl more readily than T.N.T., as little as 0.001 grm. often being effective and 0.1 grm. invariably so. In the case of T.N.T. the minimum charge under a loading pressure of 200 atmos. is 0.23 grm., and with a pressure of 400 atmos. about 0.15 grm. By using a suitable mixture of the two explosives as a base charge with a fulminate-chlorate primer, about half as much fulminate is required for a cap of given strength. The insensitiveness of T.N.T. to slightly moist fulminate makes it an unsuitable base charge.

—C. A. M.

## PATENTS.

**Explosives.** J. A. Marin. Fr. Pat. 478,351, April 12, 1915. Under Int. Conv., Mar. 3, 1914.

An explosive in crystalline form is obtained by the interaction of glycerin with basic lead chlorate, or of lead oxide or hydroxide with a solution of lead chlorate in glycerin. Compounds of mannitol, sugar, dextrose, dextrin, or tannin with basic lead chlorate may be made in a similar manner; or these substances may be made to react with glycerin and basic lead chlorate. One or more combustible substances may also be mixed with the crystalline product.—C. A. M.

**Explosive powder; Powerful — and method of manufacturing it. Smokeless powder and method of making it.** J. M. Brown. Fr. Pats. (A) 478,383 and (B) 478,384, Apr. 13, 1915. Under Int. Conv., Mar. 3, 1915.

(A) A SOLUTION of, say, 8 to 10% of a resin and an oil (boiled linseed oil) is mixed with an alkali chlorate (70 to 76% of sodium chlorate), a cereal flour (about 22%) is added to the mixture, with or without the addition of about 4% of charcoal, and the mass is pressed and granulated. (B) A solution of, say, 8 to 16% of resin and linseed oil (preferably boiled oil) is mixed with an alkali perchlorate (60 to 70% of ammonium perchlorate), sulphur (5 to 10%) added, and the mixture incorporated with a cereal flour (about 23%). The mass is left to harden and is then granulated.

—C. A. M.

**Explosives; Manufacture of —.** F. Steppes, Munich. Ger. Pat. 290,156, Aug. 11, 1915.

By treating the diazo derivatives of more or less highly nitrated, substituted derivatives of diphenylamine or its homologues with nitric acid, stable products are obtained which are not more sensitive to percussion than picric acid.—A. S.

**Smokeless powder; Manufacture of stable —.** G. Spica, Venice. Ger. Pat. 291,578, Dec. 2, 1914.

A MIXTURE of collodion-cotton, nitroglycerin, and phenanthrene is treated in a roller apparatus at a temperature of at least 100° C., then immersed in a bath of warm water saturated with nitroglycerin, and afterwards again rolled under the same conditions as before.—A. S.

**Explosive charges; Method of firing —.** C. A. Baldus and A. Kowatsch, Charlottenburg. Ger. Pat. 292,554, June 23, 1914. Addition to Ger. Pat. 282,780 (see Fr. Pat. 474,508; this J. 1915, 1118).

ACCORDING to the chief patent, liquid air was added to a cartridge containing a mixture of 60% of kieselguhr and 40% of petroleum. By adding aluminium, magnesium, or the like to this mixture, the velocity of detonation and the explosive force are considerably increased.—A. S.

**Fireworks; Preparation of mixtures for —.** J. J. Braun, Schmalkalden. Ger. Pat. 293,582, Oct. 9, 1915.

LIQUID air is used in conjunction with combustible or incombustible substances which by themselves are not inflammable or explosive. Suitable mixtures are chalk 70, and soot 30%; coke dust 80, and soot 20%; and powdered glass 60, and soot 40%.—A. S.

**Explosives; Moulding press for —.** F. Quartieri, Milan, Italy. U.S. Pat. 1,200,982, Oct. 10, 1916. Date of appl., Sept. 1, 1914.

See Eng. Pat. 19,645 of 1914; this J., 1915, 1118.

## XXIII.—ANALYSIS.

**Filter paper; Abnormal adsorption [of hydrochloric acid] by —.** R. R. Murray. J. Phys. Chem., 1916, 20, 621—624.

FIVE grms. of shredded filter paper was shaken with 100 c.c. of standard hydrochloric acid solution, and allowed to stand for 1 hour to 10 days, and the filtered liquid then titrated. It was found that the adsorption of the acid increased with the concentration of the solution. For example, 9.6 mgrms. of HCl per grm. of paper was adsorbed from a solution containing 0.986 grm.-equiv. of acid per litre, whilst 2.9 mgrms. was adsorbed from a solution containing 0.489 grm.-equiv. per litre. When the filter paper was left in contact with the acid solutions for 7 to 10 days it underwent some change, which reduced the adsorption capacity to less than half its original value. The abnormal results obtained by Evans (J. Phys. Chem., 1906, 10, 290) must be attributed to errors due to his choice of indicator. When phenolphthalein was used as indicator the apparent adsorptions were much lower than when methyl orange was the indicator in titrating the residual acid solution.—C. A. M.

**Calcium chloride, sodium hydroxide, and potassium hydroxide; Efficiency of — as drying agents.** G. P. Baxter and H. W. Starkweather. J. Amer. Chem. Soc., 1916, 38, 2038—2041.

THE aqueous vapour pressures of the lowest hydrates of the following substances have, respectively, at 0°, 25°, and 50° C., values in millimetres as under:  $\text{CaCl}_2$ , 0.07, 0.34, and 1.34;  $\text{NaOH}$ , 0.04, 0.15, 1.15;  $\text{KOH}$ , not measurable in first two cases, 0.007 at 50° C. The considerable tem-

perature coefficients with calcium chloride and sodium hydroxide, and the great efficiency of potassium hydroxide, which at 25°C. is as efficient as sulphuric acid, are noteworthy. The weights of residual water in a litre of a gas dried at 25°C. by the various drying agents are given as follows for comparison:  $\text{CaCl}_2$ , 0.36 mgrm.;  $\text{ZnCl}_2$ , 0.8 mgrm.;  $\text{NaOH}$ , 0.16 mgrm.;  $\text{KOH}$ , 0.002 mgrm.;  $\text{H}_2\text{SO}_4$ , 0.003 mgrm.—G. F. M.

*Anions of group 1: Systematic separation of the —. Anions whose silver salts are insoluble in nitric acid.* H. C. P. Weber and H. A. Winkelmann. *J. Amer. Chem. Soc.*, 1916, 38, 2000–2013.

A PROCEDURE is described for the systematic separation of the anions of group 1 in the order  $\text{Fe}(\text{CN})_6^{4-}$ ,  $\text{Fe}(\text{CN})_6^{3-}$ ,  $\text{CN}^-$ ,  $\text{CNS}^-$ ,  $\text{Cl}^-$ ,  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{S}^{2-}$ . From the solution slightly acid with nitric acid, zinc nitrate precipitates ferro- and ferricyanide; these are further separated by dissolving in sodium hydroxide and adding 5% ammonium nitrate solution, which precipitates zinc ferrocyanide, leaving ammonium ferricyanide in solution. From the original filtrate silver nitrate precipitates the remaining ions, and the silver salts are digested with mercuric acetate and acetic acid, when the cyanide passes into solution as a complex mercury cyanide; its identity is confirmed by conversion into thiocyanate. The remaining silver salts are boiled with alkaline sodium formate containing 8% sodium hydroxide, when the chloride and thiocyanate are alone reduced, the ions passing into solution as the sodium salts, from which they are re-precipitated as cuprous thiocyanate and silver chloride respectively. The residual precipitate of silver, and silver bromide, iodide, and sulphide is treated with concentrated ammonia solution and copper powder, when cuprous bromide and iodide dissolve instantly, and silver sulphide remains. On neutralising the filtrate with sulphurous acid and adding an excess of dilute sulphuric acid, cuprous iodide is precipitated, and the bromine is separated as silver bromide after adding nitric acid and boiling to expel sulphur dioxide. Finally the silver sulphide is converted into sulphate by boiling with nitric acid, and the sulphate precipitated as barium sulphate. Full data are given as to the quantitative aspect of the separation.—G. F. M.

*Phosphoric acid: Loss of — during fusion with ammonium fluoride.* W. A. Davis and J. A. Prescott. *J. Agric. Sci.*, 1916, 8, 136–138.

THE results obtained for the phosphoric acid content of salts, soils, and minerals when these are ignited with ammonium fluoride to eliminate silica as tetrafluoride, are low, probably owing to the loss of phosphorus as fluoride. No loss was observed during the subsequent ignition with sulphuric acid. The loss was greatest (over 50%) in the case of alkaline-earth phosphates, and it was less with disodium hydrogen phosphate than with potassium dihydrogen phosphate.—E. H. T.

*Diphenylamine-sulphuric acid reagent; Preparation of —.* W. Tönies. *Z. Unters. Nahr. Genussm.*, 1916, 31, 322. *J. Chem. Soc.*, 1916, 110, ii, 534.

THIS reagent may be prepared with ordinary sulphuric acid provided that the mixture is heated at 110°C. until any blue coloration due to the presence of nitric acid has disappeared. The heating expels the nitric acid and does not injure the reagent.

*Lactic acid; New method of extracting — for its determination.* E. Ohlsson. *Skand. Arch. Physiol.*, 1916, 33, 231–234. *J. Chem. Soc.*, 1916, 110, ii, 542–543.

In the estimation of lactic acid according to von

Fürth-Charnass (this *J.*, 1910, 903) as modified by Embden, the extraction with ether is a troublesome and lengthy process. For the isolation in a pure state the author finds ethyl acetate a better solvent, and when the acid is merely to be estimated, amyl alcohol is much better. The liquid containing lactic acid is saturated with ammonium sulphate, filtered after twelve hours, and mixed with 1/10-volume of 50% sulphuric acid. It is then shaken with 2 volumes of amyl alcohol, which is then freed from the acid by shaking with sodium carbonate, and used similarly for four more successive extractions of the fluid. Traces of amyl alcohol are removed from the sodium carbonate extracts by three extractions with benzene, and the estimation is then carried out in the usual way.

*Furfural [from pentoses]; A comparison of barbituric acid, thiobarbituric acid, and malonylguanidine as quantitative precipitants for —.* A. W. Dox and G. P. Plaisance. *J. Amer. Chem. Soc.*, 1916, 38, 2156–2164.

BARBITURIC acid possesses certain advantages over phloroglucinol as a precipitating agent in the determination of furfural; the precipitate is a definite condensation product of 1 mol. of the aldehyde with 1 mol. of barbituric acid, through its methylene group, with elimination of  $\text{H}_2\text{O}$ ; the reaction is more specific than with phloroglucinol, and, whereas the latter gives high results owing to hydroxymethylfurfural when sucrose is present with the pentose, barbituric acid still gives normal values. The precipitate, however, is sufficiently soluble to require a correction for solubility (1.22 mgrms. per 100 c.c.) and it is necessary to employ a large excess of the reagent (16 times the theoretical amount) if low results are to be avoided. The authors have found that thiobarbituric acid possesses the advantages without the drawbacks of barbituric acid. The precipitation in the ordinary acid distillate is quantitative at the ordinary temperature without using a large excess of the reagent; the furfural-malonylthiourea forms a flocculent, voluminous yellow precipitate which filters slowly but without practical difficulty and can be dried to constant weight at 100°C. It is practically insoluble in cold dilute acids and no correction is necessary; good results are obtained with as little as 12 mgrms. of furfural. Methylfurfural yields with thiobarbituric acid a condensation product having substantially identical properties, and it is to be inferred that methylpentoses would be quantitatively determined with the pentoses. As the products possess a perfectly definite composition, mixtures of furfural and methylfurfural could be determined from the percentages of nitrogen and sulphur in the precipitates. It is important for accurate work that the thiobarbituric acid be carefully purified; if impure, the results may show only 90–95% of the furfural and the filtrate have a red or green colour. This is attributed to the presence of ethyl cyanacetate in the ethyl malonate employed. The ethyl malonate should be subjected to repeated simultaneous saponification and esterification before being condensed with sodium ethoxide and thiourea, and the thiobarbituric acid purified by one or two recrystallisations of its sodium salt. Malonylguanidine gives a green flocculent precipitate with furfural, but its solubility is such that its use for quantitative purposes is quite out of the question.—J. F. B.

*Peroxydase purified by ultrafiltration; Reactions of —.* A. Bach. *Arch. Sci. phys. nat.*, 1916, [iv.], 42, 56–61. *J. Chem. Soc.*, 1916, 110, i, 682–683.

WHILST phenol, guaiacol, quinol, and pyrogallol were found to give the same colour reactions with



an extract of horse-radish and the same extract subjected to ultrafiltration, in presence of hydrogen peroxide, very different results were obtained with orcinol, aniline, dimethyl- and diethyl-aniline, benzidine, and *p*-phenylenediamine. When *o*-cresol and saligenin are treated with a mixture of purified peroxidase and hydrogen peroxide, a yellow colour is produced in both cases, which changes to brown and then to reddish-brown. Salicylaldehyde only reacts when the solution is made slightly alkaline with hydrogen dipotassium phosphate. Salicylic acid gives no reaction. In the oxidation of *o*-cresol and saligenin, formic acid is produced, but no appreciable amount of carbon dioxide could be detected. Ethyl alcohol is not attacked. It is considered more probable that ethyl alcohol is oxidised by a mixture than by a specific "alcoholoxydase."

*New method for purification of colloidal solutions.* Wegelin. See I.

*New method of testing naphthalene wash oils.* Wohl. See II.

*Determination of phenol in crude phenols from tar.* Masse and Leroux. See III.

*Colours produced by resorcinol in solutions of certain salts and their use for the detection of resorcinol in presence of other phenols.* Krauskopf and Ritter. See III.

*Staining of tissues with the simplest dyestuffs, and their fixation.* Skraup. See VI.

*Volumetric determination of chlorides in presence of thiocyanates.* Bruckmiller. See VII.

*Attack [by reagents] of French, Bohemian, and German glass.* Nicolardot. See VIII.

*New method for the production of accurately dimensioned glass tubes.* Lambris. See VIII.

*Freezing point of mercury.* Wilhelm. See X.

*Quantitative determination of silica in soils.* Von Horváth. See XVI.

*Ammoniacal nitrogen of peats and humus soils.* Ellis and Morison. See XVI.

*Supposed precipitation of reducing sugars by basic lead acetate.* Davis. See XVII.

*Approximate determination of the sugar content of wine.* Pritzker. See XVIII.

*Detection of artificial colouring matters in wine.* Kreis. See XVIII.

*Use of the iodic acid-starch reaction in the control of vinegar and wine.* Jeanprêtre. See XVIII.

*An examination of certain methods for the study of proteolytic action.* Sherman and Neun. See XIXa.

*Detection and determination of hydrocyonic acid in beans.* Guignard. See XIXa.

*Determination of fat in cocoa.* Kreis. See XIXa.

*Detection of beetroot in chicory.* Collin. See XIXa.

*Determination of calcium in ash of forage plants and animal carcasses.* Kuzirian. See XIXa.

*Determination of hydrogen sulphide in water.* Winkler. See XIXb.

*Modification of the Pratt method for the determination of citric acid.* Willaman. See XX.

#### PATENT.

*Polariscopes.* L. Laurance and H. O. Wood, London. Eng. Pat. 14,320, Oct. 9, 1915.

A POLARISCOPE of the reflection type, for the examination of spectacle lenses, crystals, gems, etc., is formed of a dark box with a source of light at one end, and a tubular support at the other containing a converging lens or lens-system, and an "eye-rest" at the extreme end of the support. Two black reflectors are arranged at suitable angles at each end of the box, and between these are perforated screens between which the substance to be examined is placed. The parts are arranged so that of the two principal foci of the lens, one lies approximately midway between the reflectors or screens, and the other approximately at the principal plane of the observer's eye when the latter is upon the "eye-rest."—B. N.

#### XXIV.—MISCELLANEOUS ABSTRACTS.

*Pyrogallol, ferrous sulphate, and fructose [lævulose]; Influence of strong salt solutions on the spontaneous oxidation of —.* C. G. MacArthur. J. Phys. Chem., 1916, 20, 545–553.

A DEFINITE quantity of the substance to be oxidised was mechanically shaken with 50 c.c. of *N*/10 sodium hydroxide solution containing in solution quantities of salt in concentrations of  $\frac{1}{2}$  to 4 *M*. The flask was provided with a thermometer and was connected with a manometer, and the amount of oxygen absorbed was determined by the negative pressure measured by the manometer. The results showed that higher manometer readings are obtained, with an increase in time, for all concentrations of salt. The effect of sodium chloride, potassium chloride, and potassium nitrate upon the rate of oxidation of pyrogallol, ferrous sulphate, and lævulose is about the same. Sodium bromide, however, reduces the solubility of oxygen more than the above salts, and therefore causes a greater decrease in the rate of oxidation, whilst sodium sulphate and magnesium chloride affect both the oxygen solubility and the rate of oxidation more than sodium bromide. In all cases an increase in the amount of salt causes a decrease in the rate of oxidation. Except in the case of lævulose in dilute salt solutions the rate of oxidation is parallel to the solubility of oxygen.—C. A. M.

#### Trade Report.

France: Prohibited exports.

A FRENCH Presidential Decree, dated October 26th, prohibits the exportation from France of the following:—Formic acid, oxalic acid, albumin, benzyl benzoate, ethyl benzoate, borate of lime,



carbon chloride, carbon tetrachloride, chlorine compounds, colchicum and its preparations, coffee substitutes, dextrin, dyeing extracts, kaolin, manure of all kinds, "chemical matches," products containing essence of turpentine, radium and its salts, silica bricks, spirits and liqueurs, volatile or essential oils.

Of the above, however, all with the exception of oxalic acid, albumin, borate of lime, carbon chloride, and chlorine compounds may be exported without special authorisation to the United Kingdom, the British Dominions, Colonies, and Protectorates, and certain other countries.

#### Prohibited Exports.

By virtue of an Order in Council, dated November 17th, the exportation of Cocaine and its salts and preparations to all destinations is prohibited. The heading, "Emery, corundum, etc.," in the Proclamation of May 16th last (see this Journal, 1916, 621), is altered to "Emery and corundum and manufactures thereof, carborundum, alundum, crystalon, and all other artificial abrasions and manufactures thereof." The heading "Casin and preparations thereof" is transferred from Class 3 to Class 2, the heading "Varnishes, spirit, containing gum" is replaced by the heading "Varnishes not otherwise prohibited," and a new heading is added, viz., "Oils, essential (except turpentine oil)."

#### Books Received.

**A SYSTEM OF PHYSICAL CHEMISTRY.** By W. C. MCC. LEWIS, M.A., D.Sc. 2 volumes. Longmans, Green and Co. London. Price 9s. net each volume.

THE study of physical chemistry in this country has hitherto scarcely received the attention which its importance deserves both from the purely scientific and the technical standpoints. There is scarcely an industry connected with chemistry for which the principles of this branch of the subject are not of importance, and the future progress of certain of our industries will depend in no small measure on the skill and intelligence shown in applying the methods of physical chemistry to the problems involved. Any book which facilitates the acquirement of this knowledge deserves a hearty welcome.

The book under review belongs to the series of text books on physical chemistry edited by Sir William Ramsay, but differs from the other members of the series (which are devoted to special topics) in affording a general and fairly comprehensive view of the subject. It is not an easy matter to give within a moderate compass an adequate and connected presentation of what has now become a very extensive branch of chemistry, and it is satisfactory to be able to state that Prof. Lewis has been conspicuously successful in his task. The author has a thorough and up-to-date knowledge of his subject, commands a lucid style, and shows excellent judgment in the selection and arrangement of material. The clearness and care with which the thermodynamical principles of the subject are explained and illustrated deserve special praise.

The method of presentation adopted is as follows. Physico-chemical phenomena are divided into those exhibited by material systems when in a state of equilibrium and those exhibited by

systems which have not reached a state of equilibrium. The phenomena exhibited by systems in equilibrium and not in equilibrium are treated first from the classic kinetic standpoint only (Volume I.), then independently from the thermodynamic standpoint, and finally from the standpoint of thermodynamics and statistical mechanics (Volume II.). This system has undoubtedly much to recommend it, more particularly as regards the postponement of the difficult thermodynamical treatment until the student has obtained a good grasp of the subject from the simpler kinetic standpoint. Most of us are acquainted with works on physical chemistry which, although in most respects excellent, repel at the outset all except the mathematically-minded student by plunging into difficult thermodynamical reasoning in the first few pages.

Volume I. (kinetic theory) deals with molecular magnitudes and allied phenomena, equations of state, chemical equilibrium in homogeneous and heterogeneous systems from the kinetic standpoint, and reaction velocity. The treatment is very similar to that in other books and calls for no special remark except that attention should be directed to one commendable feature, namely the reproduction of parts of the classic papers on the subject in the investigators' own words. Volume II., Part II., in which physico-chemical phenomena are considered from the standpoint of thermodynamics, contains full accounts of some important recent advances, such as Smits' theory of allotropy, Donnan's theory of membrane equilibria and Nernst's heat theorem. Volume II., Part III., contains a good account of photo-chemistry and a full and excellent account of the theory of energy-quanta. There is little in the book that calls for adverse criticism, even in details. The style on the whole is good, but split infinitives are met with rather frequently. "Hantzsch" instead of "Hantzsch" occurs three times on p. 317 and also in the index, and so is presumably not a printer's error. The book is provided with excellent subject and author indexes, and therefore should be very useful for reference.

GEORGE SENTER.

**THE MINERAL RESOURCES OF TEXAS.** By W. B. PHILLIPS. Bulletin of the University of Texas No. 365. Published by the University, Austin, Texas. 302 pages and 40 illustrations.

**TRATTATO DI CHIMICA ANALITICA APPLICATA.** Metodi e norme per l'esame chimico dei principali prodotti industriali ed alimentari. Vol. I. Di V. VILLAVECCHIA, Direttore dei Laboratori Chimici della Gabelle, con la collaborazione dei G. FABRIS, A. BIANCHI, G. ARMANI, G. ROSSI, G. SILVESTRI, G. BOSCO, R. BELASIO, F. BARONI, ed A. CAPELLI. U. Hoepli, Milan. XX+622 pages, 9½×6½ in., with 55 illustrations. Price L.12.50.

THIS is the first volume of a work on technical chemical analysis to be completed in two volumes. The present volume contains chapters on the examination of: waters (20 pages); chemical products, such as acids, alkalis, salts, etc. (133 pages); fertilisers (30 pages); cements, plasters, etc. 31 pages; metals and alloys (184 pages); fuels (24 pages); coal tar and tar products (23 pages); mineral oils and their derivatives (47 pages); fats and oils (84 pages); and commercial products from fats and oils (36 pages). The methods recommended have, in most cases, been thoroughly tested in the Italian Customs Laboratory, and found trustworthy; and with few exceptions only one, or two, methods are given for a particular determination.

